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(54) **NOX OCCLUSION-REDUCTION TYPE TERNARY CATALYST AND APPARATUS FOR CLEANING EXHAUST GAS USING SAME**

(57)Abstract:
PROBLEM TO BE SOLVED: To enhance the NOx removing performance of an NOx occlusion- reduction type ternary catalyst by allowing a prescribed multiple oxide to coexist suitably with noble metallic elements.
SOLUTION: The objective ternary catalyst contains a noble metal carrying powder obtd. by carrying one or more noble metals selected from the group comprising Pt, Pd and Rh on a porous carrier, a powdery multiple oxide represented by the formula (where Ln is one or more selected from the group comprising La, Ce, Nb and Sm, B is one or more selected from the group comprising Fe, Co, Ni and Mn, $0<\alpha<1$ and $0<\beta<4$) and carbonates of one or more metals selected from the group comprising Mg, Ca, Sr, Ba, Na, K and Cs. The amt. of the ceria and the ceria-contg. multiple oxide in the ternary catalyst is about 5-30 g/l. The catalyst has enhanced NOx removing performance.

$$Ln\alpha BO\beta$$

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CLAIMS

[Claim(s)]

[Claim 1] In the NOx occlusion reduction type three way component catalyst which absorbs NOx in exhaust gas, emits absorbed NOx in theoretical air fuel ratio or a rich ambient atmosphere, and carries out reduction processing by lean atmosphere The noble-metals support powder which supported at least one sort of noble metals chosen from the group which consists of platinum, palladium, and a rhodium to porosity support, and degree type **LnalphaBObeta ... ** (Ln in a formula) at least one sort chosen from the group which consists of La, Ce, Nd, and Sm, and B show at least one sort chosen from the group which consists of Fe, Co, nickel, and Mn, and are 0< alpha<1 and 0< beta<4. The NOx occlusion reduction type three way component catalyst characterized by containing the multiple oxide powder expressed and the carbonate of at least one sort of metals chosen from the group which consists of Mg, calcium, Sr, Ba, Na, K, and Cs.

[Claim 2] The above-mentioned multiple oxide powder is degree type **(Ln1-deltaCdelta) alphaBObeta... ** (Ln in a formula) as for at least one sort chosen from the group which consists of La, Ce, Nd, and Sm, and C, Ba, and/or K and B show at least one sort chosen from the group which consists of Fe, Co, nickel, and Mn, and 0< delta<1, 0.8< alpha<1, and beta are the amounts of oxygen with which are satisfied of the valence of each element. The NOx occlusion reduction type three way component catalyst according to claim 1 characterized by what is expressed.

[Claim 3] The NOx occlusion reduction type three way component catalyst according to claim 1 or 2 characterized by for the above-mentioned noble-metals support powder supporting palladium and/or a rhodium to porosity support, and changing.

[Claim 4] The NOx occlusion reduction type three way component catalyst according to claim 1 or 2 characterized by for the above-mentioned noble-metals support powder supporting palladium to porosity support, and changing.

[Claim 5] In the exhaust gas purge which carried out sequential arrangement of a three way component catalyst and the NOx occlusion reduction type three way component catalyst from the upstream of an exhaust air system The above-mentioned three way component catalyst contains at least one sort chosen from the group which consists of platinum, palladium, and a rhodium. And the exhaust gas purge with which the amounts of a multiple oxide including Seria included in this three way component catalyst and Seria are per [5-30g] 1l. of catalysts, and the above-mentioned NOx occlusion reduction type three way component catalyst is characterized by being an NOx occlusion reduction type three way component catalyst given in any one term of claims 1-4.

[Claim 6] combustion -- the target air-fuel ratio of gaseous mixture -- immediately after [from Lean] theoretical air fuel ratio or immediately after switching richly -- combustion -- the exhaust gas purge according to claim 5 which carries out feedback control of the air-fuel ratio of gaseous mixture, and is characterized for the exhaust air air-fuel ratio in the downstream by theoretical air fuel ratio or making it richly reversed from Lean from the above-mentioned NOx occlusion reduction type three way component catalyst.

[Claim 7] A 1st air-fuel ratio detection means for it to be arranged at the upstream and to detect an exhaust air air-fuel ratio from the above-mentioned NOx occlusion reduction type three way component catalyst, Have a 2nd air-fuel ratio detection means for it to be arranged at the downstream and to detect an exhaust air air-fuel ratio from this NOx occlusion reduction type three way component catalyst, and it sets to a normal state further. the exhaust air air-fuel ratio detected with the above-mentioned 1st air-fuel ratio detection means -- being based -- combustion -- with the 1st air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio The target air-fuel ratio of gaseous mixture sets theoretical air fuel ratio or immediately after switching richly from Lean. combustion -- the exhaust air air-fuel ratio detected with the above-mentioned 2nd air-fuel ratio detection means -- being based -- combustion -- the exhaust gas purge according to claim 5 or 6 characterized by adding the 2nd air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio, and changing.

[Claim 8] the above-mentioned 2nd air-fuel ratio feedback means -- combustion -- the exhaust gas purge according to claim 6 or 7 with which the target air-fuel ratio of gaseous mixture is characterized by the output of the above-mentioned 2nd air-fuel ratio detection means and the output of the above-mentioned 1st air-fuel ratio detection means performing [immediately after theoretical air fuel ratio or immediately after switching richly] feedback control from Lean until they become equal.

[Claim 9] the above-mentioned 2nd air-fuel ratio feedback means -- combustion -- the exhaust gas purge according to claim 6 or 7 with which the target air-fuel ratio of gaseous mixture is characterized [immediately after theoretical air fuel ratio or immediately after switching richly] by performing feedback control until it becomes a predetermined value by the ratio of the output of the above-mentioned 1st air-fuel ratio detection means, and the output of the above-mentioned 2nd air-fuel ratio detection means from Lean.

[Translation done.]

* NOTICES *

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1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] The hydrocarbon in the exhaust gas with which this invention is discharged by internal combustion engines, such as an automobile (a gasoline, diesel) and a boiler it is hereafter called "HC" -- a carbon monoxide (it is hereafter called "CO" --) and nitrogen oxides (it is hereafter called "NOx" --) The exhaust gas purge which used the NOx occlusion reduction type three way component catalyst and it which are purified is started. Further in a detail It is related with the exhaust gas purge which has arranged the NOx occlusion reduction type three way component catalyst concerning the NOx occlusion reduction type three way component catalyst and exhaust gas path which raised the rate of NOx purification in lean atmosphere, and raised the rate of NOx purification.
[0002]
[Description of the Prior Art] In recent years, from the exhaustion problem and global warming issue of petroleum resources, the demand of a low-fuel-consumption automobile is increasing and development of a lean combustion automobile attracts attention to the gasoline automobile.
[0003] By this lean combustion automobile, although the exhaust air air-fuel ratio became the high hyperoxia ambient atmosphere (henceforth "lean atmosphere") of an oxygen density from theoretical air fuel ratio (henceforth "SUTOIKI") at the time of lean combustion transit, if the three way component catalyst usual by lean atmosphere was used, since the cleaning effect of NOx would become inadequate, even if it became lean atmosphere, development of the catalyst which can purify NOx was desired.
[0004] The NOx occlusion reduction type three way component catalyst with the function which carries out reduction processing of NOx to which NOx in exhaust gas was adsorbed by lean atmosphere, and it stuck in the oxygen-deficiency ambient atmosphere (henceforth a "rich ambient atmosphere") where an oxygen density is lower than SUTOIKI or it is proposed so that it may be represented by the catalyst (JP,5-168860,A) which supported platinum and a lanthanum to porosity support as opposed to such a request.
[0005] Moreover, the engine which formed this NOx occlusion reduction type three way component catalyst in the exhaust air system is indicated by JP,7-139397,A, and the exhaust gas purge which has arranged the three way component catalyst, respectively to the upstream and the downstream of an NOx occlusion reduction type three way component catalyst is further indicated by JP,8-270440,A at it.
[0006]
[Problem(s) to be Solved by the Invention] However, even if it used the conventional NOx occlusion reduction type three way component catalyst, the technical problem that the purification engine performance of NOx might become inadequate in addition occurred. moreover, NOx by which the NOx occlusion reduction type three way component catalyst was adsorbed in the Lean region -- combustion -- the air-fuel ratio of gaseous mixture being emitted SUTOIKI or by switching richly, and, although HC and CO are needed in case it is returned If the usual three way component catalyst is arranged from an NOx occlusion reduction type three way component catalyst to the upstream, since HC and CO will be consumed by oxidation reaction of this three way component catalyst in an exhaust air system, The technical problem that HC and CO which are needed for reduction processing of NOx were no longer enough supplied to an NOx occlusion reduction type three way component catalyst occurred.
[0007] In order to supply HC and CO required to carry out reduction processing of NOx emitted from an NOx occlusion reduction type three way component catalyst in such a situation, the technique of raising a rich degree was taken, but since the capacity which absorbs or emits NOx according to exhaust gas temperature or a degradation condition changes, an oxygen rich degree may raise beyond the need and the technical problem that the purification engine performance of HC and CO gets worse conversely also occurred in an NOx occlusion reduction type three way component catalyst.
[0008] The place which this invention is made in view of the technical problem which such a technique has, and is made into the purpose It is in offering the NOx occlusion reduction type three way component catalyst which is excellent in the purification engine performance of NOx in lean atmosphere. Moreover, it is in offering the exhaust gas purge which can improve the rate of NOx purification also when an exhaust air air-fuel ratio switches from the Lean region to SUTOIKI or a rich region, and can control aggravation of the purification engine performance of HC and CO in a rich region to the minimum.
[0009]
[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned technical problem should be solved, this invention persons by making a predetermined multiple oxide and a predetermined noble-metals element live together appropriately etc. That the NOx purification engine performance of an NOx occlusion reduction type three way component catalyst improves, by reducing the amount of components which contributes to the oxygen storage capacity in the three way component catalyst arranged from the NOx occlusion reduction type three way component catalyst to the exhaust air system upstream, etc. HC and CO which are needed in order to carry out reduction processing of NOx are enough supplied to an NOx occlusion reduction type three way component catalyst, and an exhaust air air-fuel ratio -- being based -- combustion -- by establishing the air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio etc., it came to complete a header and this invention for the ability of aggravation of the purification engine performance of HC and CO of an NOx occlusion reduction type three way component catalyst to be suppressed to the minimum.
[0010] Namely, the NOx occlusion reduction type three way component catalyst of this invention In the NOx occlusion reduction type three way component catalyst which absorbs NOx in exhaust gas, emits absorbed NOx in theoretical air fuel ratio or a rich ambient atmosphere, and carries out reduction processing by lean atmosphere The noble-metals support powder which supported at least one sort of noble metals chosen from the group which consists of platinum, palladium, and a rhodium to porosity support, and degree type **LnalphaBObeta ... ** (Ln in a formula) at least one sort chosen from the group which consists of La, Ce, Nd, and Sm, and B show at

least one sort chosen from the group which consists of Fe, Co, nickel, and Mn, and are 0< alpha<1 and 0< beta<4. It is characterized by containing the multiple oxide powder expressed and the carbonate of at least one sort of metals chosen from the group which consists of Mg, calcium, Sr, Ba, Na, K, and Cs.

[0011] Moreover, the exhaust gas purge of this invention uses an NOx occlusion reduction type three way component catalyst, and a three way component catalyst and an NOx occlusion reduction type three way component catalyst are set from the upstream of an exhaust air system to the exhaust gas purge which carried out sequential arrangement. The above-mentioned three way component catalyst contains at least one sort chosen from the group which consists of platinum, palladium, and a rhodium. And the amounts of a multiple oxide including Seria included in this three way component catalyst and Seria are per [5-30g] 1l. of catalysts, and the above-mentioned NOx occlusion reduction type three way component catalyst is characterized by being the NOx occlusion reduction type three way component catalyst mentioned above.

[0012] Furthermore, the suitable gestalt of the exhaust gas purge of this invention A 1st air-fuel ratio detection means for it to be arranged at the upstream and to detect an exhaust air air-fuel ratio from the above-mentioned NOx occlusion reduction type three way component catalyst, Have a 2nd air-fuel ratio detection means for it to be arranged at the downstream and to detect an exhaust air air-fuel ratio from this NOx occlusion reduction type three way component catalyst, and it sets to a normal state further. the exhaust air air-fuel ratio detected with the above-mentioned 1st air-fuel ratio detection means -- being based -- combustion -- with the 1st air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio The target air-fuel ratio of gaseous mixture sets theoretical air fuel ratio or immediately after switching richly from Lean. combustion -- the exhaust air air-fuel ratio detected with the above-mentioned 2nd air-fuel ratio detection means -- being based -- combustion -- it is characterized by adding the 2nd air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio, and changing.

[0013]

[Function] The NOx occlusion reduction type three way component catalyst of this invention emits and purifies NOx to which NOx was absorbed by lean atmosphere and it stuck in SUTOIKI or a rich ambient atmosphere.

[0014] In lean atmosphere, NOx is adsorbed by carbonates, such as magnesium, calcium, strontium, barium, sodium, a potassium, and caesium, after activating with the noble-metals support powder and multiple oxide powder which supported noble metals to porosity support. Here, since noble-metals support powder and a multiple oxide are powdered and it lives together, the flow of exhaust gas becomes smooth and high activity is acquired.

[0015] In SUTOIKI or a rich ambient atmosphere, HC reacts with NOx by which the complex (henceforth "Complex B") applied to the component B of a multiple oxide by the function as solid acid was powerfully adsorbed, and the complex (henceforth "Complex A") concerning the component A of the multiple oxide which exists in the near (it corresponds to Ln etc. by ** or ** formula) was adsorbed. Thereby, desorption of NOx by which the NOx occlusion reduction type three way component catalyst was adsorbed is carried out from an NOx occlusion reduction type three way component catalyst, and the post reduction processing is made.

[0016] The NOx purification engine performance of the NOx occlusion reduction type three way component catalyst of this invention also sets after heat durability. High one A multiple oxide is the inside of the above-mentioned ** or ** type, and alpha (it is hereafter called "A site rate".) to an existing [multiple oxide / the noble-metals support powder and multiple oxide which supported noble metals to porosity support are powdered, and] list. It is based on little perovskite type structure, and since solid phase reaction with other components in Complex A and Complex B, and a catalyst (for example, alumina) was avoided, it guesses.

[0017] Although desorption of NOx which stuck to the NOx occlusion reduction type three way component catalyst is carried out and the post reduction processing is made in the exhaust gas purge of the internal combustion engine of this invention when an exhaust air air-fuel ratio switches from lean atmosphere to SUTOIKI or a rich ambient atmosphere Since the amount of components which contributes to the oxygen storage capacity in the three way component catalyst arranged from the NOx occlusion reduction type three way component catalyst at the exhaust air system upstream is reduced, Since the amount of HC and CO which are consumed by oxidation reaction of a three way component catalyst decreases and HC and CO required for reduction processing are enough supplied to an NOx occlusion reduction type three way component catalyst, the rate of purification of NOx improves.

[0018] Moreover, when an exhaust air air-fuel ratio switches from the Lean region to a rich region using the output signal of the air-fuel ratio detection means installed in the exhaust air system upstream and the downstream from an NOx occlusion reduction type three way component catalyst, it sets. If the time amount held richly is controlled, since NOx to which it stuck in the Lean region will fully be emitted and reduction processing will be carried out, without being dependent on the degradation condition and operating temperature of an NOx occlusion reduction type three way component catalyst, The rate of purification of NOx not only improves, but it is not necessary to supply HC and CO beyond the need, and aggravation of the purification engine performance of HC and CO in a rich region is suppressed to the minimum.

[0019]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. First, it explains per NOx occlusion reduction type three way component catalyst of this invention. The NOx occlusion reduction type three way component catalyst of this invention contains noble-metals support powder, multiple oxide powder, and a carbonate.

[0020] Here, noble-metals support powder can support noble metals to porosity support, and can mention an alumina as an example of representation of porosity support. As porosity support, a heat-resistant high thing is desirable, and specific surface area can use most suitably 50-300cm activated alumina it is [activated alumina] about 2/g.

[0021] Moreover, although especially noble metals can be supported in order to secure the function of the three way component catalyst in SUTOIKI, and they can specifically mention the combination of platinum, palladium or rhodiums, and such arbitration, its combination of palladium or a rhodium and palladium, and a rhodium is desirable, and its palladium is the most desirable. In addition, as for these noble metals, at least the part should just be supported by porosity support.

[0022] The multiple oxide powder mentioned above is degree type LnalphaBObeta... It is expressed by **. Here, Ln shows the combination of a lanthanum, a cerium, neodium or samarium, and such arbitration among ** type, and B shows the combination of iron, cobalt, nickel or manganese, and such arbitration. As Ln, a lanthanum and neodium are desirable and cobalt and manganese of B are desirable. A site rate has the good range of 0< alpha<1, and 0.8< alpha<0.9 is desirable. In addition, in ** type, if it deviates from the range of 0< alpha<1 and 0< beta<4, since NOx activation ability will fall, it is not desirable.

[0023] Moreover, the suitable example of this multiple oxide powder is degree type (Ln1-deltaCdelta) alphaBObeta... It is expressed by **. Here, Ln and B show the same thing as the above among ** type, and C shows the combination of barium or a potassium, barium, and a potassium. As Ln, the combination of a lanthanum, neodium, or a lanthanum and neodium is desirable, and a lanthanum is the most desirable. As B, cobalt is desirable. The range of 0< delta<1 is good, the structural stability of an oxide gets worse and delta is not desirable, if delta deviates from the range of 0< delta<1. The range of alpha of 0.8< alpha<1 is good, and 0.8< alpha<0.9 is desirable. If the crystal structure will become unstable if alpha is smaller than 0.8, and alpha becomes large and approaches 1 from 0.9,

since it becomes easy to react with an alumina etc. and may be able to stop being able to maintain the crystal structure, it is not desirable. In addition, beta is the amount of oxygen with which are satisfied of the valence of each element.
[0024] ** Or although it is desirable that each components of all have compound-ized as for the multiple oxide of **, the target operation is acquired even when the part has compound-ized. Moreover, although the impurity contained in a configuration element may mix into the multiple oxide of ** or **, a problem will not be produced if it is not the amount which bars the operation. for example, the inside of the barium among the elements which constitute a multiple oxide -- ****** rare ****** also interferes [strontium / a cerium neodium, samarium, etc. / neither a hafnium nor sulfur] into ****** rare ******** and a zirconium into ****** rare **** and a lanthanum.
[0025] The carbonate of barium and strontium is [that what is necessary is just a carbonate concerning magnesium, calcium, strontium, barium, sodium, a potassium or caesium, and the mixture of such arbitration as a carbonate mentioned above] desirable. In addition, although it relates to the manufacture approach of the multiple oxide concerning the NOx occlusion reduction type three way component catalyst mentioned later, especially the class of salt in magnesium, calcium, strontium, barium, sodium, a potassium or caesium, and the metal salt water solution of such mixture is not limited, and a nitrate, acetate, a carbonate, a hydroxylation salt, a hydrochloride, etc. are mentioned. Moreover, even if it is the water solution which consists of one sort, or the water solution which mixed two or more sorts of metals, it does not interfere.
[0026] Moreover, in an NOx occlusion reduction type three way component catalyst, it is desirable to consider the content of noble-metals support powder and a multiple oxide as per [catalyst 1L / 200-300g]. Since the dispersibility of noble-metals support powder and a multiple oxide can be improved and the diffusibility to Complex B and Complex A of exhaust gas can be raised by considering as such a content, it is thought that a lot of NOx purification is attained.
[0027] Although the NOx occlusion reduction type three way component catalyst of this invention uses noble-metals support powder, multiple oxide powder, and a carbonate as an indispensable component like ****, it is also possible to add other components in addition to this. For example, additives, such as rare earth compounds, such as a cerium and a lanthanum, and a zirconium, may be added as used with the three way component catalyst from the former, in order to raise the thermal resistance of an alumina. Moreover, in order to reinforce the function as a three way component catalyst, Seria which may add the ingredient used for the three way component catalyst from the former, for example, has an oxygen storage function, the barium which eases HC adsorption poisoning to noble metals, the zirconia which contributes to the heat-resistant improvement in a rhodium may be added.
[0028] Although non-support can also be used for it, when the NOx occlusion reduction type three way component catalyst of this invention mentioned above purifies the exhaust gas of an automobile, it is desirable to support and use for integral-construction mold support. As integral-construction mold support, the monolith support which consists of a heat-resistant ingredient can use suitably metal things, such as ceramics, such as cordierite, and ferrite system stainless steel, preferably.
[0029] In the manufacture approach of the multiple oxide concerning the NOx occlusion reduction type three way component catalyst of this invention For example, the water solution of the metal salts (a nitrate, a carbonate, a citric acid, hydrochloride, etc.) of each component is prepared. Depending on the case, add precipitation reagents (ammonia, ammonium carbonate, etc.) to this, settlings are made to generate, there is a method of drying and calcinating these solutions or settlings and obtaining multiple oxide powder, a part of each component [at least] compound-izes by these processes, and it becomes a thing corresponding to the purpose. However, even if it is not necessarily limited to the above-mentioned approach and is approaches other than the above, the manufacture approach of the above-mentioned multiple oxide is enough if the multiple oxide to mean is formed.
[0030] If the NOx occlusion reduction type three way component catalyst of this invention mentioned above is suitable to purify the exhaust gas of the lean burn engine vehicle by which an air-fuel ratio is repeatedly changed in 10-50 and it is used under such an environment, in order to carry out reduction processing and to carry out desorption of NOx to which NOx was adsorbed, and it is SUTOIKI or a rich ambient atmosphere, and stuck by lean atmosphere, the high NOx purification engine performance is obtained. Furthermore, lean atmosphere is 15-50 and SUTOIKI or the rich ambient atmosphere of the suitable range is 10-14.8.
[0031] Next, with reference to a drawing, it explains to a detail about the exhaust gas purge of this invention. This exhaust gas purge is equipment which used the NOx occlusion reduction type three way component catalyst of this invention mentioned above.
[0032] Drawing 1 is a block diagram showing an example of the basic configuration of the exhaust gas purge using the NOx occlusion reduction type three way component catalyst concerning this invention. In this drawing, sequential arrangement of the 1st air-fuel ratio detection means 4, a three way component catalyst 2, the NOx occlusion reduction type three way component catalyst 3, and the 2nd air-fuel ratio detection means 5 is carried out from the upstream of an internal combustion engine's 1 exhaust air system with this purge. Moreover, 1st air-fuel ratio feedback means 6a and 2nd air-fuel ratio feedback means 6b are connected possible [data communication] to the above-mentioned air-fuel ratio detection means 4 and 5. Feedback control of the air-fuel ratio of gaseous mixture is carried out to a target air-fuel ratio. the exhaust air air-fuel ratio with which 1st air-fuel ratio feedback means 6a was detected with the 1st air-fuel ratio detection means 4 -- being based -- combustion -- 2nd air-fuel ratio feedback means 6b -- combustion -- the exhaust air air-fuel ratio with which the target air-fuel ratio of gaseous mixture was detected with the 2nd air-fuel ratio detection means 5 SUTOIKI or immediately after switching richly from Lean -- being based -- combustion -- feedback control of the air-fuel ratio of gaseous mixture is carried out to a target air-fuel ratio.
[0033] Drawing 2 is the system configuration Fig. showing an example of the exhaust gas purge using the NOx occlusion reduction type three way component catalyst concerning this invention. In addition, the same sign is substantially given to the same member with what was shown in drawing 1 , and the explanation is omitted. In drawing 2 , a sign 7 shows a fuel injection valve, 8 shows the exhaust pipe, and casing which built in casing and the NOx occlusion reduction type three way component catalyst 3 which built in the fuel injection valve 7, the internal combustion engine 1, and the three way component catalyst 2 is open for free passage through this exhaust pipe 8. Moreover, 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a which detect an exhaust air air-fuel ratio are arranged on the upstream of a three way component catalyst 2, and the lower stream of a river of the NOx occlusion reduction type three way component catalyst 3, respectively, and the output of 1st air-fuel ratio sensor 4a, 2nd air-fuel ratio sensor 5a, and a fuel injection valve 7 is connected to the exhaust pipe 8 at the control unit 6 which achieves the function of 1st air-fuel ratio feedback means 6a mentioned above and 2nd air-fuel ratio feedback means 6b.
[0034] although the amount of Seria (CeO_2) which is the component which contributes to oxygen storage capacity is adjusted and it is specifically 50 - 60 g/L in the conventional three way component catalyst in a three way component catalyst 2 here -- receiving -- 5-30g/L -- it is preferably adjusted to 5 - 15 g/L.
[0035] Moreover, the NOx occlusion reduction type three way component catalyst 3 is a catalyst concerning this invention mentioned above. As mentioned above [when an exhaust air air-fuel ratio is Lean, absorb NOx in exhaust gas, are the catalyst to which an exhaust air air-fuel ratio carries out reduction processing of this absorbed NOx SUTOIKI or when rich, and], although an alumina is used as a support base material On this support base material, at least one sort chosen from caesium, the alkali metal represented by the potassium, and the alkaline earth metal represented by barium and at least one sort chosen from noble metals like platinum,

palladium, and a rhodium are supported.
[0036] Although the sensor which detects an exhaust air air-fuel ratio based on the oxygen density in exhaust gas as 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a can be used, you may be the SUTOIKI sensor which detects only theoretical air fuel ratio, and may be the broader-based air-fuel ratio sensor which can detect an exhaust air air-fuel ratio in a wide area.
[0037] In a control unit 6, a target air-fuel ratio is determined according to a service condition, fuel oil consumption (injection pulse width) calculates so that the gaseous mixture of the target air-fuel ratio may be formed, and the fuel-injection signal over a fuel injection valve 7 is determined. In addition, as a target air-fuel ratio, it has composition which SUTOIKI and not only Rich but Lean can set up.
[0038] Moreover, in a control unit 6, setting up the air-fuel ratio feedback correction factor (control input) for amending fuel oil consumption by proportional-plus-integral control etc. is performed so that the exhaust air air-fuel ratio usually detected by 1st air-fuel ratio sensor 4a may be brought close to a target air-fuel ratio (this function is equivalent to 1st air-fuel ratio feedback means 6a.). In addition, a switch of Lean of a target air-fuel ratio to SUTOIKI or RITCHIHE Even if it is carried out by the service condition (change of acceleration, and a load and rotation) and also is under the condition to which the Lean air-fuel ratio is originally set as a target air-fuel ratio When it is presumed that the NOx absorbed amount in the NOx occlusion reduction type three way component catalyst 3 has reached threshold value, it is a setup which can perform rich control temporarily, and a switch in a temporary rich region for carrying out reduction processing of NOx is also included.
[0039] Furthermore, a control unit 6 is equivalent to the function in which a target air-fuel ratio performs the above-mentioned feedback control of air-fuel ratio according to output change of 2nd air-fuel ratio sensor 5a SUTOIKI or immediately after switching richly from Lean and in which get down as like and 2nd air-fuel ratio feedback means 6b achieves this function. An example of the feedback control by this 2nd air-fuel ratio feedback means 6b is shown in drawing 3 .
[0040] In drawing 3 , first, it is step 11 (it abbreviates to "S11" hereafter.), and it is distinguished for Air Fuel Ratio Control for carrying out reduction processing of NOx whether it is the need. And if it is judged that Air Fuel Ratio Control for carrying out reduction processing of NOx is required, a target air-fuel ratio will be switched to a rich ambient atmosphere from lean atmosphere (S12).
[0041] Next, the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a is detected (S13), and it is judged whether the output of 2nd air-fuel ratio sensor 5a is more rich than the output of 1st air-fuel ratio sensor 4a (S14). When the output of 2nd air-fuel ratio sensor 5a is not more rich than the output of 1st air-fuel ratio sensor 4a, an air-fuel ratio is made rich until the output of 2nd air-fuel ratio sensor 5a becomes more rich than the output of 1st air-fuel ratio sensor 4a. And if the output of 2nd air-fuel ratio sensor 5a becomes more rich than the output of 1st air-fuel ratio sensor 4a, it will progress to step 15 and an air-fuel ratio will be reversed to Lean (refer to drawing 6).
[0042] The reason for processing the above-mentioned steps 13-15 is as follows. That is, while reduction processing was made with the NOx occlusion reduction type three way component catalyst and NOx is desorbed from the NOx occlusion reduction type three way component catalyst, oxidation and reduction are performed by HC and CO which were supplied in order to make an air-fuel ratio rich, respectively, and the output of 2nd air-fuel ratio sensor 5a is maintained near SUTOIKI. Then, if the amount of NOx desorbed from an NOx occlusion reduction type three way component catalyst decreases, balance collapses, the output of 2nd air-fuel ratio sensor 5a moves in the rich direction, and when the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a becomes equal, it will be thought that the desorption of NOx was completed (refer to drawing 5). Since the output of the 2nd air-fuel ratio sensor becomes more rich than the output of the 1st air-fuel ratio sensor after an appropriate time, what is necessary will be just to perform reversal to Lean like ****.
[0043] As mentioned above, NOx which the NOx occlusion reduction type three way component catalyst absorbed at the time of Lean operation can fully be desorbed by reversing a target air-fuel ratio to Lean based on the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a, since rich. Under the present circumstances, it becomes possible to desorb NOx effectively for a short time rather than reducing Seria (CeO2) which is the oxygen storage component contained in the three way component catalyst 2 arranged at the upstream (refer to drawing 7). Moreover, since a target air-fuel ratio is rich, even if an NOx absorbed amount changes with temperature etc. or an NOx absorbed amount and the amount of oxygen storage have change by (refer to drawing 8) and aging by reversing RINHE based on the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a, the desorption conditions of NOx corresponding to an NOx absorbed amount can be set up.
[0044] Next, other examples of feedback control of air-fuel ratio are explained. Drawing 4 is a flow chart which shows other examples of control by 2nd air-fuel ratio feedback means 6b. In this drawing, first, it is step 21 and it is distinguished for Air Fuel Ratio Control for carrying out reduction processing of NOx whether it is the need. if it is judged that this Air Fuel Ratio Control is required -- threshold [from operational status (engine rotation, fuel oil consumption)] S -- a map -- detecting (S22) -- subsequently -- a target air-fuel ratio -- the theoretical air fuel ratio from Lean -- or it is switched richly (S23).
[0045] Next, it distinguishes whether at step 24, the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a was detected, and the ratio of the output of 2nd air-fuel ratio sensor 5a and the output of 1st air-fuel ratio sensor 4a became more than threshold S (S25). When the ratio of the appearance mosquito of 2nd air-fuel ratio sensor 5a and the output of 1st air-fuel ratio sensor 4a is smaller than threshold S, it makes an air-fuel ratio rich until the output of 2nd air-fuel ratio sensor 5a becomes more rich than the output of 1st air-fuel ratio sensor 4a. When it judges that the ratio of the output of 2nd air-fuel ratio sensor 5a and the output of 1st air-fuel ratio sensor 4a became more than threshold S, it progresses to step 26 and Lean is made to reverse an air-fuel ratio (refer to drawing 9).
[0046] As mentioned above, according to this example, NOx which the NOx occlusion reduction type three way component catalyst absorbed at the time of Lean operation can fully be desorbed by reversing a target air-fuel ratio to Lean like the example shown in drawing 3 , based on the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a, since rich. Moreover, NOx can be effectively desorbed for a short time rather than it reduces Seria (CeO2) which is the oxygen storage component contained in the three way component catalyst arranged at the upstream. Furthermore, since a target air-fuel ratio is rich, even if an NOx absorbed amount changes with temperature etc. by reversing RINHE or an NOx absorbed amount and the amount of oxygen storage have change by aging based on the ratio of the output of 1st air-fuel ratio sensor 4a and 2nd air-fuel ratio sensor 5a, it is also possible to set up the desorption conditions of NOx corresponding to an NOx absorbed amount.
[0047] In addition, although considered as the square wave as showed the configuration of a rich spike to drawing 10 , respectively in the example shown in drawing 3 and drawing 4 , as shown in drawing 11 , even if it makes the configuration of a rich spike into a triangular wave, the same effectiveness as **** is acquired.
[0048]
[Example] Hereafter, although an example, the example of a comparison, and the example of a trial explain this invention to a detail, this invention is not limited to these examples.
[0049]

(1) manufacture of an NOx occlusion reduction type three way component catalyst and a characteristic test (example 1) palladium nitrate water solution were boiled, and it sank into activated-alumina powder, it calcinated at 400 degrees C after desiccation and among air for 1 hour, and palladium support alumina powder (powder A) was obtained. The palladium concentration of this powder was 5.6 % of the weight. Moreover, the citric acid was added to a carbonic acid lanthanum and the mixture of cobalt carbonate, it calcinated at 700 degrees C after desiccation, and powder (powder B) was obtained. This powder was a lanthanum / cobalt =0.8/1 in the metal atomic ratio. Preferential grinding of powder A600g, powder B300g, and 900g of water obtained as mentioned above was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.

[0050] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and coat layer weight 150 g/L-support was obtained. After sinking the barium acetate water solution into the obtained 150 g/L-support and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the catalyst of the example 1 which supported the barium carbonate was acquired. Thus, the amount of barium of the acquired catalyst of this example was 20 g/L in oxide conversion.

[0051] The presentation of the catalyst of the following examples and the example of a comparison is collectively shown in Table 1 at this example list.

[0052] (Example 1 of a comparison) Except having replaced Powder B with the activated alumina, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0053] (Example 2 of a comparison) Except having not performed barium support, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0054] (Example 2) Except having set La of Powder B to Ce, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0055] (Example 3) Except having set La of Powder B to Nd, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0056] (Example 4) Except having set Co of Powder B to Mn, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0057] (Example 5) Except having set Co of Powder B to Fe, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0058] (Example 6) Except having set Co of Powder B to nickel, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0059] (Example 7) Except having set Ba to K, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0060] (Example 8) Except having set Ba to Sr, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0061] (Example 9) Except having set Ba to Cs, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0062] (Example 10) Except having used Ba as the mixture (it being 1:1 at the weight ratio of oxide conversion) of Cs and Mg, the same actuation as an example 1 was repeated, and the catalyst of this example was acquired.

[0063] (Example 11) It sank into the activated alumina, the nitric-acid rhodium water solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and rhodium support powder (powder C) was obtained. The rhodium concentration of this powder was 2.0 % of the weight. It sank into the activated alumina, the dinitrodiammine platinum solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and platinum support powder (powder D) was obtained. The platinum concentration of this powder was 4.0 % of the weight. Preferential grinding of powder C106g obtained as mentioned above, powder D265g, powder B300g, 229g of activated-alumina powder, and the 900g of the water was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.

[0064] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C for 1 hour, and coat layer weight 150 g/L-support was obtained. After sinking the barium acetate water solution into the obtained 150 g/L-support and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the catalyst of the example 11 which supported the barium carbonate was acquired. Thus, the amount of barium of the acquired catalyst of this example was 20 g/L in oxide conversion.

[0065]

[Table 1]

	貴金属 g/L	複合酸化物組成		炭酸塩元素
		元素	α	
実施例1	Pd=5.6	La, Co	0.8	Ba
比較例1	↑	なし	↑	Ba
比較例2	↑	La, Co	↑	なし
実施例2	↑	Ce, Co	↑	Ba
実施例3	↑	Nd, Co	↑	Ba
実施例4	↑	La, Mn	↑	Ba
実施例5	↑	La, Fe	↑	Ba
実施例6	↑	La, Ni	↑	Ba
実施例7	↑	La, Co	↑	K
実施例8	↑	↑	↑	Sr
実施例9	↑	↑	↑	Cs
実施例10	↑	↑	↑	Cs+Mg
実施例11	Pt=1.77 Rh=0.35	↑	↑	Ba

[0066] (Catalyst characteristic test 1) It examined by the following approach about the catalyst of each example acquired as mentioned above. The obtained result is shown in Table 2.
(The durable approach) The exhaust air system of an engine with a displacement of 4400 cc was equipped with the catalyst of each example, catalyst inlet temperature was made into 700 degrees C, and it operated for 50 hours.
(The evaluation approach) The exhaust air system of an engine with a displacement of 2000 cc was equipped with the catalyst of each example, it operated so that A/F=11.0 might be repeated in 10 seconds and for 30 seconds might be repeated for A/F=22 by turns, and catalyst inlet temperature was made into 350 degrees C, and it asked for the total invert ratio of this 1 cycle switch operation.
[0067]
[Table 2]

	転化率%		
	HC	CO	NO
実施例1	95	100	76
比較例1	96	100	48
比較例2	96	100	48
実施例2	96	100	79
実施例3	96	100	76
実施例4	96	100	76
実施例5	96	100	75
実施例6	96	100	77
実施例7	92	100	82
実施例8	96	100	72
実施例9	90	100	83
実施例10	96	100	85
実施例11	95	100	69

[0068] (Example 12) It sank into activated-alumina powder, the palladium nitrate water solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and palladium support alumina powder (powder E) was obtained. The palladium concentration of this powder was 5.0 % of the weight. Moreover, the citric acid was added to the mixture of a carbonic acid lanthanum, a barium carbonate, and cobalt carbonate, it calcinated at 700 degrees C after desiccation, and powder (powder F) was obtained. This powder was lanthanum / barium / cobalt =2/7/10 in the metal atomic ratio. Furthermore, it sank into Powder F, the dinitrodiammine platinum solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and the platinum support powder F (powder G) was obtained. The platinum concentration of this powder was 5.0 % of the weight. Preferential grinding of powder E544g, powder G342g, 12g of activated-alumina powder, and 902g of water obtained as mentioned above was thrown in and carried out to the

magnetic ball mill, and slurry liquid was obtained.
[0069] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the catalyst of the example 12 which supported coat layer weight 105 g/L was acquired. Thus, the acquired catalyst of this example contains 64g and 40g of powder G for per [catalyst 1L] and Powder E. In addition, the presentation of the catalyst of the following examples and the example of a comparison is collectively shown in Table 3 at this example list.
[0070] (Example 3 of a comparison) The same actuation as an example 12 was performed, and palladium support alumina powder (powder E) was obtained. Moreover, it sank into activated-alumina powder, the dinitrodiammine platinum solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and platinum support alumina powder (powder H) was obtained. The platinum concentration of this powder was 5.0 % of the weight. Preferential grinding of powder E544g, powder H342g, 12g of activated-alumina powder, and 902g of water obtained as mentioned above was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0071] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the example 3 of a comparison which supported coat layer weight 105 g/L was acquired. Thus, the acquired catalyst of this example contains 64g and 40g of powder H for per [catalyst 1L] and Powder E.
[0072] (Example 13) Except having set 171g and activated-alumina powder to 456g, and having set [Powder E] water to 898g for 272g and Powder G, the same actuation as an example 12 was repeated, and the example 13 which supported coat layer weight 210 g/L was acquired. Thus, the acquired catalyst of this example contains 64g and 40g of powder F for per [catalyst 1L] and Powder E.
[0073] (Example 14) It sank into activated-alumina powder, the palladium nitrate water solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and palladium support alumina powder (powder E') was obtained. The palladium concentration of this powder E' was 2.5 % of the weight. Moreover, it sank into Powder F, the dinitrodiammine platinum solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and platinum support alumina powder (powder G') was obtained. The platinum concentration of this powder G' was 2.5 % of the weight. Preferential grinding of E'545g of powder obtained as mentioned above, G'343g of powder, 24g of activated-alumina powder, and the 888g of the water was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0074] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the example 14 which supported coat layer weight 210 g/L was acquired. Thus, the acquired catalyst of this example contains 125g and 79g powder G' for per [catalyst 1L] and powder E'.
[0075] (Example 15) Except having set 229g and activated-alumina powder to 308g, and having set [powder E'] water to 900g for 363g and powder G', the same actuation as an example 14 was repeated, and the example 15 which supported coat layer weight 315 g/L was acquired. Thus, the acquired catalyst of this example contains 127g and 80g powder G' for per [catalyst 1L] and powder E'.
[0076] (Example 16) Except having set Ba of Powder F to Cs, the same actuation as an example 15 was repeated, and the catalyst of this example was acquired.
[0077] (Example 17) It sank into activated-alumina powder, the nitric-acid rhodium water solution was calcinated at 400 degrees C after desiccation and among air for 1 hour, and rhodium support alumina powder (powder I) was obtained. Rh concentration of this powder I was 4.0 % of the weight. Preferential grinding of obtained powder I33g, E'422g of powder, G'229g of powder, 190g of activated-alumina powder, and the 924g of the water was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0078] After having made this slurry liquid adhere to the nature monolith support of a KODI light (1.3L, 400 cels), removing the slurry of the surplus in a cel in airstream and drying at 130 degrees C, it calcinated at 400 degrees C among air for 1 hour, and the example 17 which supported coat layer weight 315 g/L was acquired.
[0079] (Example 18) Except having set Ba of Powder F to Cs, the same actuation as an example 17 was repeated, and the catalyst of this example was acquired.
[0080]
[Table 3]

	貴金属	貴金属量 (g/L)	コート層重量 (g/L)	炭酸塩元素
実施例12	Pd、Pt	Pd=3. 2 Pt=2. 0	105	La、Ba、Co
比較例3	Pd、Pt	Pd=3. 2 Pt=2. 0	105	La、Ba、Co
実施例13	Pd、Pt	Pd=3. 2 Pt=2. 0	210	La、Ba、Co
実施例14	Pd、Pt	Pd=3. 2 Pt=2. 0	210	La、Ba、Co
実施例15	Pd、Pt	Pd=3. 2 Pt=2. 0	315	La、Ba、Co
実施例16	Pd、Pt	Pd=3. 2 Pt=2. 0	315	La、Cs、Co
実施例17	Pd、Pt、Rh	Pd=3. 8 Pt=2. 0 Rh=0. 5	315	La、Ba、Co
実施例18	Pd、Pt、Rh	Pd=3. 8 Pt=2. 0 Rh=0. 5	315	La、Cs、Co

[0081] (Catalyst characteristic test 2) It examined by the following approach about the catalyst of the examples 12-17 acquired as mentioned above and the example 3 of a comparison. The obtained result is shown in Table 4. In addition, each figure in Table 4 is expressed with a percentage.
(The durable approach) The same approach as the example 1 of a trial was performed.
(The evaluation approach) The same approach as the example 1 of a trial was performed.
[0082]
[Table 4]

	HC	CO	NOx
実施例12	95	100	72
比較例3	93	100	45
実施例13	96	100	78
実施例14	96	100	82
実施例15	97	100	84
実施例16	94	100	92
実施例17	97	100	88
実施例18	95	100	94

[0083] (2) Except having replaced the performance test (example 19) barium of the exhaust gas purge using an NOx occlusion reduction type three way component catalyst with caesium, the same actuation as an example 11 was repeated, and the catalyst of this example was acquired.
[0084] (Example 20) First, support baking of 8 % of the weight of ceriums, 4 % of the weight of zirconiums, and the 4 % of the weight of the lanthanums was carried out at activated-alumina powder, and cerium zirconium lanthanum alumina powder was obtained. The palladium nitrate water solution was sprayed agitating this powder, and the palladium support alumina powder which calcinated after that and supported 1.16 % of the weight of palladium was obtained. Thus, preferential grinding of obtained 900g of palladium support alumina powder, and nitric-acid acidity alumina sol 900g and 1200g of 10 % of the weight water solutions of acetic acids was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0085] This slurry liquid was applied to the nature monolith support of a KODI light, and in airstream, the slurry of the surplus in a cel was removed, and it dried, and calcinated at 400 degrees C for 1 hour, and the monolith support of coat layer weight 142 g/L was obtained.
[0086] Next, the nitric-acid rhodium water solution was sprayed on activated-alumina powder, and the rhodium support alumina which calcinated after that and supported 1.0 % of the weight of rhodiums was obtained. Thus, preferential grinding of obtained 114g of rhodium support alumina powder, the 279g of the above-mentioned palladium support alumina powder, and nitric-acid acidity alumina sol 400g and 900g of 10 % of the weight water solutions of acetic acids was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0087] This slurry liquid was applied to the monolith support of the above-mentioned coat layer weight of 142g / L, after removing the slurry of the surplus in a cel and drying in airstream, it calcinated at 400 degrees C for 1 hour, and the example 20 which carried out support of coat layer weight 213 g/L was acquired.
[0088] (Example 21) Except having replaced 8 % of the weight of ceriums with 4 % of the weight of ceriums, the same actuation as an example 20 was repeated, and the catalyst of this example was acquired.
[0089] (Example 22) The 1.19 % of the weight support alumina powder of palladium which sprayed the palladium nitrate water solution on activated-alumina powder, calcinated after that first, and supported 1.19 % of the weight of palladium was obtained. Apart from this, in the water solution containing a zirconium nitrate and a cerium nitrate, the aqueous ammonia solution was added, generated sediment was calcinated and the zirconia cerium multiple oxide was obtained. Thus, preferential grinding of obtained 772g of 1.19 % of the weight support alumina powder of palladium and 214g of zirconia cerium multiple oxides, and the 1200g of the 10 % of the weight water solutions of acetic acids was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0090] This slurry liquid was applied to the nature monolith support of a KODI light, and in airstream, the slurry of the surplus in a cel was removed, and it dried, and calcinated at 400 degrees C for 1 hour, and the monolith support of coat layer weight 140 g/L was obtained.
[0091] Next, the nitric-acid rhodium water solution was sprayed on activated-alumina powder, and the rhodium support alumina which calcinated after that and supported 1.0 % of the weight of rhodiums was obtained. The 1.07 % of the weight support alumina powder of palladium which sprayed the palladium nitrate water solution on activated-alumina powder, calcinated after that apart from this, and supported 1.07 % of the weight of palladium was obtained. Thus, preferential grinding of obtained 114g of rhodium support alumina powder, 306g of 1.07 % of the weight support alumina powder of palladium and the 240g of the above-mentioned zirconia cerium multiple oxides, and the 900g of the 10 % of the weight water solutions of acetic acids was thrown in and carried out to the magnetic ball mill, and slurry liquid was obtained.
[0092] This slurry liquid was applied to the monolith support of above-mentioned coat layer weight 140 g/L, after removing the slurry of the surplus in a cel and drying in airstream, it calcinated at 400 degrees C for 1 hour, and the example 22 which supported the coat layer AUW of 210g / L was acquired.
[0093] (Example 4 of a comparison) Except having replaced 214g of zirconia cerium multiple oxides with 428g of zirconia cerium multiple oxides, and having replaced the 240g of the above-mentioned zirconia cerium multiple oxides with the 480g of the above-mentioned zirconia cerium multiple oxides, the same actuation as an example 22 was repeated, and the catalyst of this example was acquired.
[0094] (Example 5 of a comparison) Except having replaced 214g of zirconia cerium multiple oxides with 0g of zirconia cerium multiple oxides, and having replaced the 240g of the above-mentioned zirconia cerium multiple oxides with the 0g of the above-mentioned zirconia cerium multiple oxides, the same actuation as an example 22 was repeated, and the catalyst of this example was acquired.
[0095] (Equipment performance test) It examined by the following approach about the catalyst of the examples 4 and 5 of a comparison in the examples 1, 9, 11, and 19 acquired as mentioned above - 22 lists. The obtained result is shown in Table 5.
(The durable approach) The exhaust air system of an engine with a displacement of 4400 cc was equipped with the catalyst of each

example, catalyst inlet temperature was made into 700 degrees C, and it operated for 50 hours.
(The evaluation approach) All over the same passage with a displacement of 2000 cc of an engine exhaust air system, as shown in Table 5, it equipped with two catalysts, it operated so that A/F=11.0 and A/F=22 might be repeated by turns, and catalyst inlet temperature was made into 450 degrees C of upstream, and 350 degrees C of downstream, and it asked for the total invert ratio of this 1 cycle switch operation.
[0096]
[Table 5]

	三元触媒	NOx吸蔵還元型三元触媒	ηHC（%）	ηNOx（%）
比較例6	比較例4	実施例9	98	78
実施例23	実施例20	実施例9	98	88
実施例24	実施例21	実施例9	98	92
実施例25	実施例22	実施例9	97	85
比較例7	比較例5	実施例9	85	90
実施例26	実施例21	実施例1	98	84
実施例27	実施例21	実施例11	95	90
実施例28	実施例21	実施例19	95	88

[0097] When the amount of a multiple oxide including Seria and Seria uses the three way component catalyst which are per [5-30g] 1l. of catalysts from the result of Table 5 (examples 23-28) Although the invert ratio of HC is good when a three way component catalyst with more amounts of a multiple oxide including Seria and Seria than 30g per 1l. of catalysts is used to each the invert ratio of HC and the invert ratio of NOx being good (example 6 of a comparison) It turned out that the invert ratio of NOx falls, and the invert ratio of HC falls although the invert ratio of NOx is good when a three way component catalyst with few amounts of a multiple oxide including Seria and Seria than 5g per 1l. of catalysts is used (example 7 of a comparison).
[0098]
[Effect of the Invention] As explained above, according to this invention, making a predetermined multiple oxide and a predetermined noble-metals element live together appropriately etc. can write, and the NOx occlusion reduction type three way component catalyst which is excellent in the NOx purification engine performance in lean atmosphere can be offered.
[0099] Moreover, reducing the amount of the component which contributes to the oxygen storage capacity in the three way component catalyst arranged at the upstream of an NOx occlusion reduction type three way component catalyst according to this invention etc. writes, when an exhaust air air-fuel ratio switches from Lean richly, sufficient HC and sufficient CO for an NOx occlusion reduction type three way component catalyst can be supplied, and the exhaust gas purge whose rate of purification of NOx improves can be offered.
[0100] furthermore -- according to this invention -- an exhaust air air-fuel ratio -- being based -- combustion -- it writes establishing the air-fuel ratio feedback means which carries out feedback control of the air-fuel ratio of gaseous mixture to a target air-fuel ratio etc., and it also becomes possible to offer the exhaust gas purge which can suppress aggravation of the purification engine performance of HC and CO to the minimum.
[0101]

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is a block diagram showing an example of the **** configuration of the exhaust gas purge using the NOx occlusion reduction type three way component catalyst concerning this invention.
[Drawing 2] It is a block diagram showing an example of the system of the exhaust gas purge using the NOx occlusion reduction type three way component catalyst concerning this invention.
[Drawing 3] It is the flow chart which shows an example of control by the 2nd air-fuel ratio feedback means of the exhaust gas purge concerning claim 8.
[Drawing 4] It is the flow chart which shows an example of control by the 2nd air-fuel ratio feedback means of the exhaust gas purge concerning claim 9.
[Drawing 5] It is drawing showing the desorption condition of an air-fuel ratio sensor output and NOx.
[Drawing 6] It is drawing showing an example of Air Fuel Ratio Control at the time of carrying out drawing 3 .
[Drawing 7] It is drawing showing the relation between the amount of Seria CeO_2, and the desorption condition of NOx.
[Drawing 8] It is drawing showing change of the NOx absorbed amount by exhaust gas temperature.
[Drawing 9] It is drawing showing an example of Air Fuel Ratio Control at the time of carrying out drawing 4 .
[Drawing 10] It is drawing showing the wave of Air Fuel Ratio Control in drawing 3 and drawing 4 .
[Drawing 11] It is drawing showing a wave-like example of Air Fuel Ratio Control.
[Description of Notations]
1 Internal Combustion Engine
2 Three Way Component Catalyst
3 NOx Occlusion Reduction Type Three Way Component Catalyst
4 1st Air-fuel Ratio Detection Means
4a The 1st air-fuel ratio sensor
5 2nd Air-fuel Ratio Detection Means
5a The 2nd air-fuel ratio sensor
6 Control Unit
6a The 1st air-fuel ratio feedback means
6b The 2nd air-fuel ratio feedback means
7 Fuel Injection Valve
8 Exhaust Pipe

[Translation done.]

* NOTICES *

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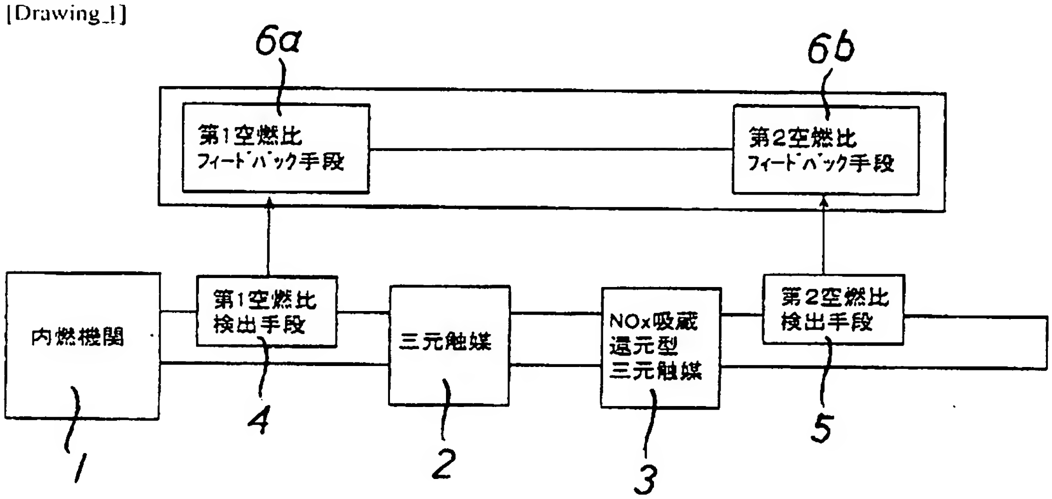
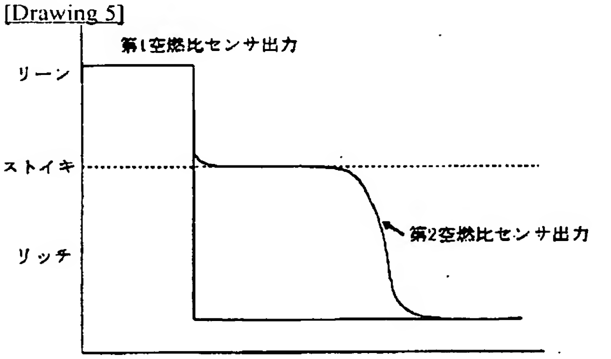
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 5]



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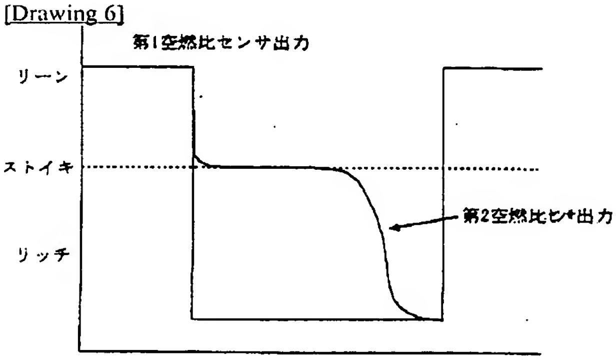

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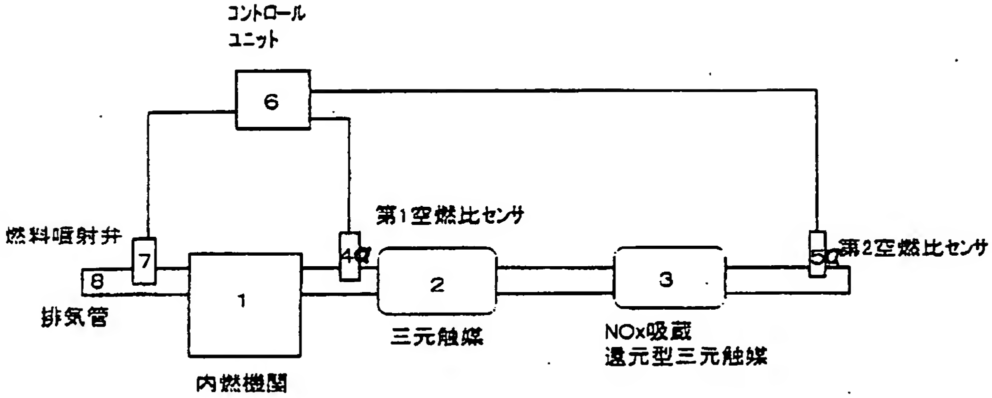

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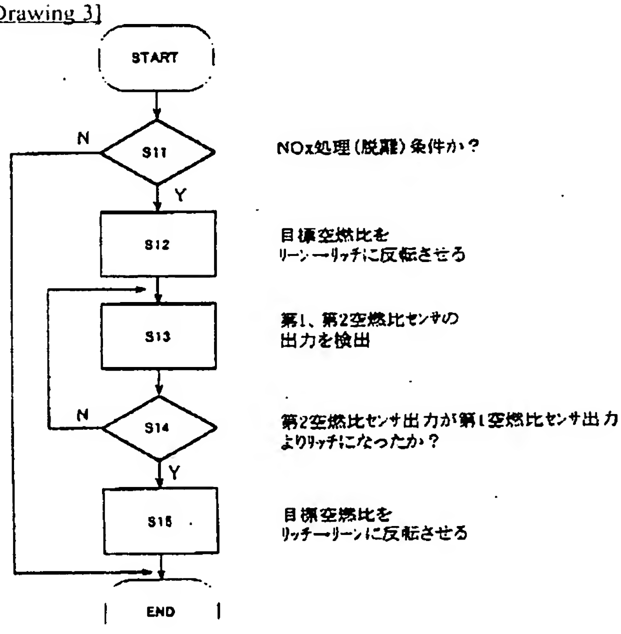

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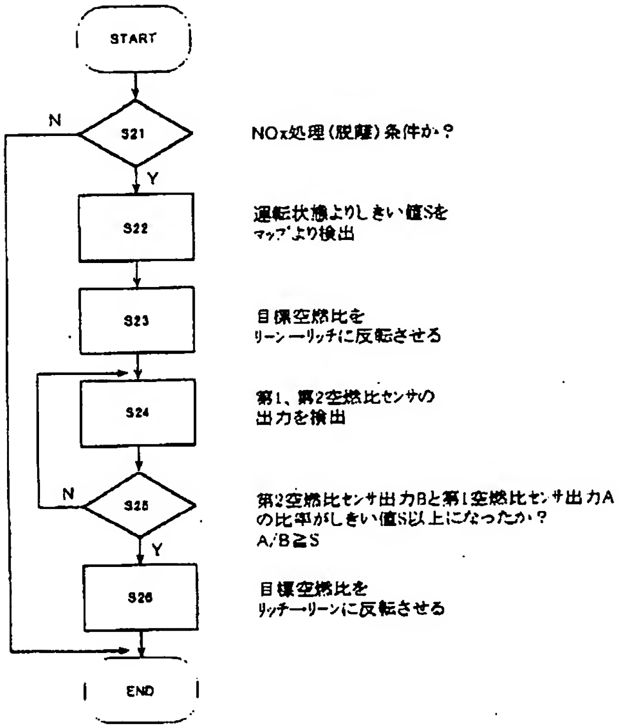

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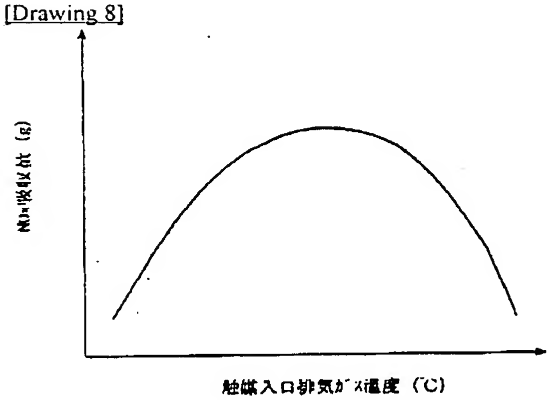

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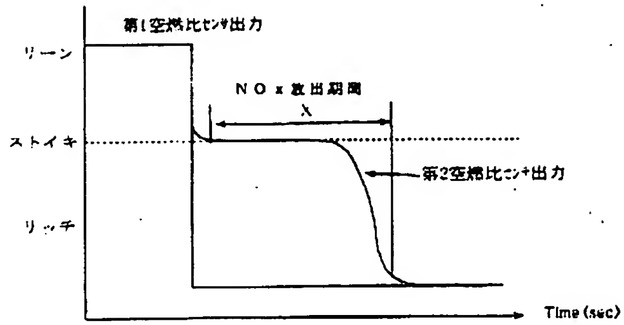

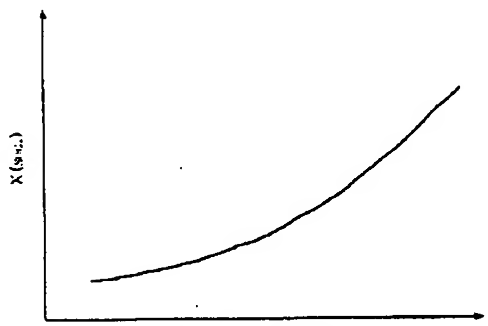

[Drawing 9]

S_{1m}				S_{nm}
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S_{11}				S_{nl}

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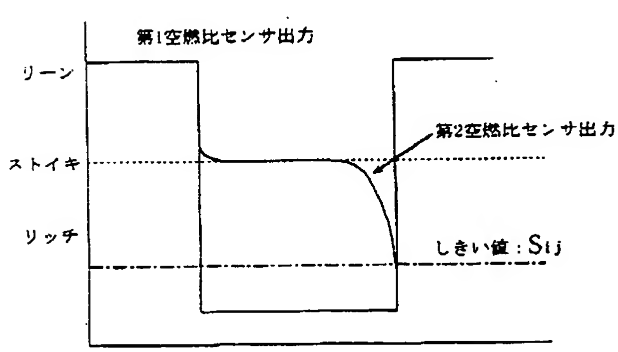
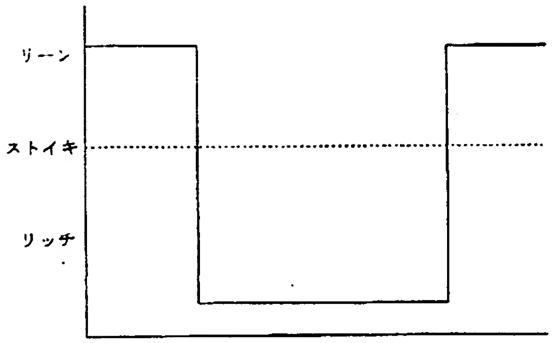


[Drawing 10]



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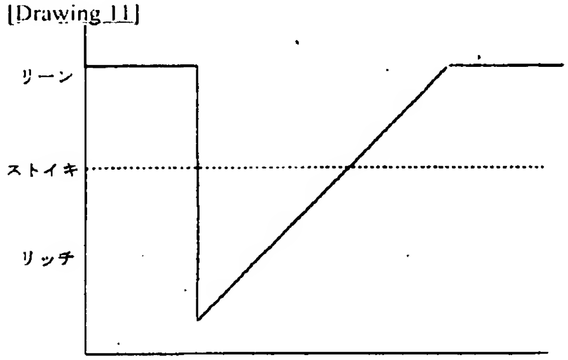

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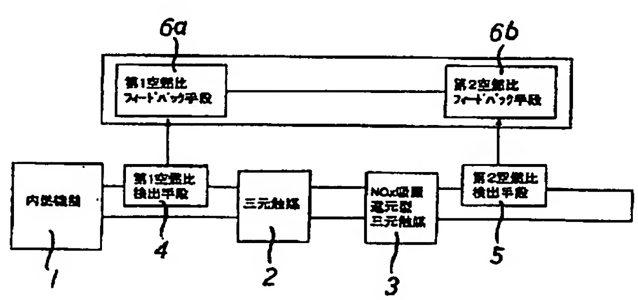
(54)【発明の名称】ＮＯｘ吸蔵還元型三元触媒及びこれを用いた排気ガス浄化装置

(57)【要約】　(修正有)

【課題】　リーン雰囲気においてＮＯｘ浄化率に優れるＮＯｘ吸蔵還元型三元触媒を提供すること及び排気空燃比がリーン雰囲気からストイキ又はリッチ雰囲気に切り換わった際にＮＯｘ浄化率が向上し、且つリッチ雰囲気においてＨＣ及びＣＯの浄化性能の悪化を最小限に抑えられる排気ガス浄化装置を提供する。

【解決手段】　内燃機関１の排気系の上流側から、第１空燃比検出部４、三元触媒２、ＮＯｘ吸蔵還元型三元触媒３、第２空燃比検出部５が順次配置され、第１空燃比検出部４で検出された排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御する第１空燃比フィードバック手段６ａ及び第２空燃比検出部で検出された排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御する第２空燃比フィードバック手段６ｂを有する。



【特許請求の範囲】

【請求項１】　リーン雰囲気で排気ガス中のＮＯｘを吸収し、吸収したＮＯｘを理論空燃比又はリッチ雰囲気で放出して還元処理するＮＯｘ吸蔵還元型三元触媒において、

白金、パラジウム、ロジウムから成る群より選ばれた少なくとも１種の貴金属を多孔質担体に担持した貴金属担持粉末と、次式①

$\mathrm{Ln}\alpha\mathrm{BO}\beta$…①

（式中のＬｎは、Ｌａ、Ｃｅ、Ｎｄ及びＳｍから成る群より選ばれた少なくとも１種、Ｂは、Ｆｅ、Ｃｏ、Ｎｉ及びＭｎから成る群より選ばれた少なくとも１種を示し、$0<\alpha<1$、$0<\beta<4$である。）で表される複合酸化物粉末と、

Ｍｇ、Ｃａ、Ｓｒ、Ｂａ、Ｎａ、Ｋ及びＣｓから成る群より選ばれた少なくとも１種の金属の炭酸塩と、を含有することを特徴とするＮＯｘ吸蔵還元型三元触媒。

【請求項２】　上記複合酸化物粉末が、次式②

$(\mathrm{Ln}_{1-\delta}\mathrm{C}\delta)\alpha\mathrm{BO}\beta$…②

（式中のＬｎは、Ｌａ、Ｃｅ、Ｎｄ及びＳｍから成る群より選ばれた少なくとも１種、Ｃは、Ｂａ及び／又はＫ、Ｂは、Ｆｅ、Ｃｏ、Ｎｉ及びＭｎから成る群より選ばれた少なくとも１種を示し、$0<\delta<1$、$0.8<\alpha<1$、βは、各元素の原子価を満足する酸素量である。）で表されることを特徴とする請求項１記載のＮＯｘ吸蔵還元型三元触媒。

【請求項３】　上記貴金属担持粉末が、パラジウム及び／又はロジウムを多孔質担体に担持して成ることを特徴とする請求項１又は２記載のＮＯｘ吸蔵還元型三元触媒。

【請求項４】　上記貴金属担持粉末が、パラジウムを多孔質担体に担持して成ることを特徴とする請求項１又は２記載のＮＯｘ吸蔵還元型三元触媒。

【請求項５】　排気系の上流側から、三元触媒とＮＯｘ吸蔵還元型三元触媒とを順次配置した排気ガス浄化装置において、

上記三元触媒が、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも１種を含有し、且つこの三元触媒に含まれるセリア及びセリアを含む複合酸化物の量が触媒１リットル当たり５～３０ｇであり、

上記ＮＯｘ吸蔵還元型三元触媒が、請求項１～４のいずれか１つの項に記載のＮＯｘ吸蔵還元型三元触媒であることを特徴とする排気ガス浄化装置。

【請求項６】　燃焼混合気の目標空燃比がリーンから理論空燃比又はリッチに切り換えられた直後に、燃焼混合気の空燃比をフィードバック制御し、上記ＮＯｘ吸蔵還元型三元触媒より下流側における排気空燃比をリーンから理論空燃比又はリッチに反転させることを特徴とする請求項５記載の排気ガス浄化装置。

【請求項７】　上記ＮＯｘ吸蔵還元型三元触媒より上流側に配置されて排気空燃比を検出する第１空燃比検出手段と、該ＮＯｘ吸蔵還元型三元触媒より下流側に配置されて排気空燃比を検出する第２空燃比検出手段とを備え、

更に、通常状態において、上記第１空燃比検出手段で検出される排気空燃比に基づき燃焼混合気の空燃比を目標空燃比にフィードバック制御する第１空燃比フィードバック手段と、燃焼混合気の目標空燃比がリーンから理論空燃比又はリッチに切り換えられた直後において、上記第２空燃比検出手段で検出される排気空燃比に基づき燃焼混合気の空燃比を目標空燃比にフィードバック制御する第２空燃比フィードバック手段とを付加して成ることを特徴とする請求項５又は６記載の排気ガス浄化装置。

【請求項８】　上記第２空燃比フィードバック手段は、燃焼混合気の目標空燃比がリーンから理論空燃比又はリッチに切り換えられた直後において、上記第２空燃比検出手段の出力と上記第１空燃比検出手段の出力とが等しくなるまでフィードバック制御を行うことを特徴とする請求項６又は７記載の排気ガス浄化装置。

【請求項９】　上記第２空燃比フィードバック手段は、燃焼混合気の目標空燃比がリーンから理論空燃比又はリッチに切り換えられた直後において、上記第１空燃比検出手段の出力と上記第２空燃比検出手段の出力との比が所定値になるまでフィードバック制御を行うことを特徴とする請求項６又は７記載の排気ガス浄化装置。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は、自動車（ガソリン、ディーゼル）、ボイラーなどの内燃機関から排出される排気ガス中の炭化水素（以下、「ＨＣ」という。）、一酸化炭素（以下、「ＣＯ」という。）及び窒素酸化物（以下、「ＮＯｘ」という。）を浄化するＮＯｘ吸蔵還元型三元触媒及びそれを使用した排気ガス浄化装置に係り、更に詳細には、リーン雰囲気でのＮＯｘ浄化率を向上させたＮＯｘ吸蔵還元型三元触媒及び排気ガス通路にかかるＮＯｘ吸蔵還元型三元触媒を配置してＮＯｘ浄化率を向上させた排気ガス浄化装置に関するものである。

【０００２】

【従来の技術】近年、石油資源の枯渇問題や地球温暖化問題から、低燃費自動車の要求が高まっており、ガソリン自動車に対しては希薄燃焼自動車の開発が注目されている。

【０００３】かかる希薄燃焼自動車では、希薄燃焼走行時において、排気空燃比が理論空燃比（以下、「ストイキ」という。）より酸素濃度の高い酸素過剰雰囲気（以下、「リーン雰囲気」という。）となるが、リーン雰囲気で通常の三元触媒を使用すると、ＮＯｘの浄化作用が不十分となるため、リーン雰囲気になってもＮＯｘを浄化できる触媒の開発が望まれていた。

【０００４】このような要望に対して、例えば、白金とランタンを多孔質担体に担持した触媒（特開平５－１６８８６０号公報）に代表されるように、リーン雰囲気で排気ガス中のＮＯｘを吸着し、ストイキ又はそれより酸素濃度が低い酸素欠乏雰囲気（以下、「リッチ雰囲気」という。）で吸着したＮＯｘを還元処理する機能を持つＮＯｘ吸蔵還元型三元触媒が提案されている。

【０００５】また、特開平７－１３９３９７号公報等には、かかるＮＯｘ吸蔵還元型三元触媒を排気系に設けた機関が開示され、更に、特開平８－２７０４４０号公報等には、ＮＯｘ吸蔵還元型三元触媒の上流側及び下流側に三元触媒をそれぞれ配置した排気ガス浄化装置が開示されている。

【０００６】

【発明が解決しようとする課題】しかしながら、従来のＮＯｘ吸蔵還元型三元触媒を用いても、なおＮＯｘの浄化性能が不十分となることがあるという課題があった。また、リーン域でＮＯｘ吸蔵還元型三元触媒に吸着されたＮＯｘが、燃焼混合気の空燃比がストイキ又はリッチに切り換わることにより放出され、還元される際には、ＨＣ及びＣＯが必要となるが、排気系において、ＮＯｘ吸蔵還元型三元触媒より上流側に通常の三元触媒を配置すると、この三元触媒の酸化反応によってＨＣ及びＣＯが消費されてしまうため、ＮＯｘの還元処理に必要となるＨＣ及びＣＯがＮＯｘ吸蔵還元型三元触媒に十分供給されなくなるという課題があった。

【０００７】このような状況において、ＮＯｘ吸蔵還元型三元触媒から放出されるＮＯｘを還元処理するのに必要なＨＣ及びＣＯを供給するためには、リッチ度合いを高める手法が採られるが、ＮＯｘ吸蔵還元型三元触媒では、排気ガス温度や劣化状態によってＮＯｘを吸収し又は放出する能力が変化するため、必要以上に酸素リッチ度合いを高めてしまうことがあり、逆にＨＣ及びＣＯの浄化性能が悪化するという課題もあった。

【０００８】本発明は、このような技術の有する課題に鑑みてなされたものであり、その目的とするところは、リーン雰囲気において、ＮＯｘの浄化性能に優れるＮＯｘ吸蔵還元型三元触媒を提供することにあり、また、排気空燃比がリーン域からストイキ又はリッチ域に切り換わった際にもＮＯｘ浄化率を向上でき、且つリッチ域においてＨＣ及びＣＯの浄化性能の悪化を最小限に抑制できる排気ガス浄化装置を提供することにある。

【０００９】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく鋭意研究した結果、所定の複合酸化物と貴金属元素とを適切に共存させることなどにより、ＮＯｘ吸蔵還元型三元触媒のＮＯｘ浄化性能が向上すること、ＮＯｘ吸蔵還元型三元触媒より排気系上流側に配置した三元触媒中の酸素ストレージ能力に寄与する成分量を低減することなどにより、ＮＯｘを還元処理するために必要となるＨＣ及びＣＯがＮＯｘ吸蔵還元型三元触媒に十分供給されること、及び排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御する空燃比フィードバック手段を設けることなどにより、ＮＯｘ吸蔵還元型三元触媒のＨＣ及びＣＯの浄化性能の悪化を最小限に抑えられることを見出し、本発明を完成するに至った。

【００１０】即ち、本発明のＮＯｘ吸蔵還元型三元触媒は、リーン雰囲気で排気ガス中のＮＯｘを吸収し、吸収したＮＯｘを理論空燃比又はリッチ雰囲気で放出して還元処理するＮＯｘ吸蔵還元型三元触媒において、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも１種の貴金属を多孔質担体に担持した貴金属担持粉末と、次式①

ＬｎαＢＯβ･･･①

（式中のＬｎは、Ｌａ、Ｃｅ、Ｎｄ及びＳｍから成る群より選ばれた少なくとも１種、Ｂは、Ｆｅ、Ｃｏ、Ｎｉ及びＭｎから成る群より選ばれた少なくとも１種を示し、$0<\alpha<1$、$0<\beta<4$である。）で表される複合酸化物粉末と、Ｍｇ、Ｃａ、Ｓｒ、Ｂａ、Ｎａ、Ｋ及びＣｓから成る群より選ばれた少なくとも１種の金属の炭酸塩と、を含有することを特徴とする。

【００１１】また、本発明の排気ガス浄化装置は、ＮＯｘ吸蔵還元型三元触媒を利用したものであり、排気系の上流側から、三元触媒とＮＯｘ吸蔵還元型三元触媒とを順次配置した排気ガス浄化装置において、上記三元触媒が、白金、パラジウム、ロジウムから成る群より選ばれた少なくとも１種を含有し、且つこの三元触媒に含まれるセリア及びセリアを含む複合酸化物の量が触媒１リットル当たり５～３０ｇであり、上記ＮＯｘ吸蔵還元型三元触媒が、上述したＮＯｘ吸蔵還元型三元触媒であることを特徴とする。

【００１２】更に、本発明の排気ガス浄化装置の好適形態は、上記ＮＯｘ吸蔵還元型三元触媒より上流側に配置されて排気空燃比を検出する第１空燃比検出手段と、該ＮＯｘ吸蔵還元型三元触媒より下流側に配置されて排気空燃比を検出する第２空燃比検出手段とを備え、更に、通常状態において、上記第１空燃比検出手段で検出される排気空燃比に基づき燃焼混合気の空燃比を目標空燃比にフィードバック制御する第１空燃比フィードバック手段と、燃焼混合気の目標空燃比がリーンから理論空燃比又はリッチに切り換えられた直後において、上記第２空燃比検出手段で検出される排気空燃比に基づき燃焼混合気の空燃比を目標空燃比にフィードバック制御する第２空燃比フィードバック手段とを付加して成ることを特徴とする。

【００１３】

【作用】本発明のＮＯｘ吸蔵還元型三元触媒は、リーン雰囲気でＮＯｘを吸収し、ストイキ又はリッチ雰囲気で吸着したＮＯｘを放出して浄化する。

【0014】リーン雰囲気において、NOxは貴金属を多孔質担体に担持した貴金属担持粉末及び複合酸化物粉末によって活性化された後、マグネシウム、カルシウム、ストロンチウム、バリウム、ナトリウム、カリウム及びセシウム等の炭酸塩に吸着される。ここで、貴金属担持粉末及び複合酸化物は粉末状で共存しているので、排気ガスの流れがスムーズになり、高い活性が得られる。

【0015】ストイキ又はリッチ雰囲気において、HCは、固体酸としての機能により複合酸化物の成分Bに係る複合体（以下、「複合体B」という。）に強力に吸着され、その近傍に存在する複合酸化物の成分A（①又は②式では、Ln等に該当）に係る複合体（以下、「複合体A」という。）に吸着されたNOxと反応する。これにより、NOx吸蔵還元型三元触媒に吸着されたNOxは、NOx吸蔵還元型三元触媒から脱着し、その後還元処理がなされる。

【0016】本発明のNOx吸蔵還元型三元触媒のNOx浄化性能が、熱耐久後においても高いのは、貴金属を多孔質担体に担持した貴金属担持粉末及び複合酸化物が粉末状で存在すること並びに複合酸化物が、上記①又は②式中、α（以下、「Aサイト割合」という。）の少ないペロブスカイト型構造を基本としており、複合体A及び複合体Bや触媒中の他の成分（例えば、アルミナ）との固相反応が回避されたためと推察される。

【0017】本発明の内燃機関の排気ガス浄化装置においては、排気空燃比がリーン雰囲気からストイキ又はリッチ雰囲気に切り換わった際、NOx吸蔵還元型三元触媒に吸着したNOxは脱着し、その後還元処理がなされるが、NOx吸蔵還元型三元触媒より排気系上流側に配置された三元触媒中の酸素ストレージ能力に寄与する成分量が低減されているため、三元触媒の酸化反応によって消費されるHC及びCOの量が減少し、還元処理に必要なHC及びCOがNOx吸蔵還元型三元触媒に十分供給されることから、NOxの浄化率が向上する。

【0018】また、NOx吸蔵還元型三元触媒より排気系上流側及び下流側に設置した空燃比検出手段の出力信号を用いて、排気空燃比がリーン域からリッチ域に切り換わった際において、リッチに保持する時間を制御すると、NOx吸蔵還元型三元触媒の劣化状態や作動温度に依存することなく、リーン域で吸着したNOxが十分に放出されて還元処理されるため、NOxの浄化率が向上するだけでなく、必要以上のHC及びCOを供給しなくてもよく、リッチ域におけるHC及びCOの浄化性能の悪化が最小限に抑えられる。

【0019】

【発明の実施の形態】以下、本発明を詳細に説明する。まず、本発明のNOx吸蔵還元型三元触媒につき説明する。本発明のNOx吸蔵還元型三元触媒は、貴金属担持粉末と、複合酸化物粉末と炭酸塩とを含有する。

【0020】ここで、貴金属担持粉末は、貴金属を多孔質担体に担持したものであり、多孔質担体の代表例としては、アルミナを挙げることができる。多孔質担体としては、耐熱性の高いものが好ましく、比表面積が50～300cm²／g程度の活性アルミナを最も好適に使用できる。

【0021】また、貴金属は、特にストイキにおける三元触媒の機能を確保するために担持するものであり、具体的には、白金、パラジウム又はロジウム及びこれらの任意の組み合わせを挙げることができるが、パラジウム又はロジウム及びパラジウムとロジウムの組み合わせが好ましく、パラジウムが最も好ましい。なお、かかる貴金属は、少なくとも一部が多孔質担体に担持されていればよい。

【0022】上述した複合酸化物粉末は、次式

$Ln\alpha BO\beta$…①

により表される。ここで、①式中、Lnは、ランタン、セリウム、ネオジウム又はサマリウム及びこれらの任意の組み合わせを示し、Bは、鉄、コバルト、ニッケル又はマンガン及びこれらの任意の組み合わせを示す。Lnとしては、ランタン、ネオジウムが好ましく、Bは、コバルト、マンガンが好ましい。Aサイト割合は、$0<\alpha<1$の範囲がよく、$0.8<\alpha<0.9$が好ましい。なお、①式において、$0<\alpha<1$、$0<\beta<4$の範囲を逸脱すると、NOx活性化能が低下するため、好ましくない。

【0023】また、この複合酸化物粉末の好適例は、次式

$(Ln_{1-\delta}C_{\delta})\alpha BO\beta$…②

により表される。ここで、②式中、Ln及びBは、上記と同じものを示し、Cは、バリウム又はカリウム、バリウムとカリウムとの組み合わせを示す。Lnとしては、ランタン若しくはネオジウム又はランタンとネオジウムとの組み合わせが好ましく、ランタンが最も好ましい。Bとしては、コバルトが好ましい。δは、$0<\delta<1$の範囲がよく、δが$0<\delta<1$の範囲を逸脱すると、酸化物の構造安定性が悪化し、好ましくない。αは、$0.8<\alpha<1$の範囲がよく、$0.8<\alpha<0.9$が好ましい。αが0.8より小さいと、結晶構造が不安定になり、αが0.9より大きくなり、1に近づくと、アルミナ等と反応しやすくなり、結晶構造を保てなくなることがあるから、好ましくない。なお、βは、各元素の原子価を満足する酸素量である。

【0024】①又は②の複合酸化物は、各成分の全てが複合化していることが好ましいが、その一部が複合化している場合でも目的とする作用は得られる。また①又は②の複合酸化物中には、構成元素に含まれる不純物が混入することがあるが、その作用を妨げる量でなければ問題は生じない。例えば、複合酸化物を構成する元素のうち、バリウム中にストロンチウムが微量含まれたり、ラ

ンタン中にセリウム、ネオジウム、サマリウムなどが微量含まれていたり、ジルコニウム中にハフニウムやイオウが微量含まれていても差し支えない。

【００２５】上述した炭酸塩としては、マグネシウム、カルシウム、ストロンチウム、バリウム、ナトリウム、カリウム又はセシウム及びこれらの任意の混合物に係る炭酸塩であればよく、バリウム、ストロンチウムの炭酸塩が好ましい。なお、後述するＮＯｘ吸蔵還元型三元触媒に係る複合酸化物の製造方法に関連するが、マグネシウム、カルシウム、ストロンチウム、バリウム、ナトリウム、カリウム又はセシウム及びこれらの混合物の金属塩水溶液における塩の種類は、特に限定されるものではなく、硝酸塩、酢酸塩、炭酸塩、水酸化塩、塩酸塩などが挙げられる。また、１種から成る水溶液でも、あるいは２種以上の金属を混合した水溶液であっても差し支えない。

【００２６】また、ＮＯｘ吸蔵還元型三元触媒においては、貴金属担持粉末と複合酸化物の含有量を触媒１Ｌ当たり２００～３００ｇとすることが好ましい。このような含有量とすることにより、貴金属担持粉末及び複合酸化物の分散性を向上でき、排気ガスの複合体Ｂ及び複合体Ａへの拡散性を高めることができるので、より多量のＮＯｘ浄化が可能になると考えられる。

【００２７】上述の如く、本発明のＮＯｘ吸蔵還元型三元触媒は、貴金属担持粉末、複合酸化物粉末及び炭酸塩を必須成分とするが、これ以外に他の成分を添加することも可能である。例えば、アルミナの耐熱性を向上させる目的で、従来から三元触媒で使用されているように、セリウム、ランタン等の希土類化合物やジルコニウムなどの添加物を加えてもよい。また、三元触媒としての機能を増強するため、従来から三元触媒に用いられている材料を添加してもよく、例えば、酸素ストレージ機能を持つセリア、貴金属へのＨＣ吸着被毒を緩和するバリウム、ロジウムの耐熱性向上に寄与するジルコニア等を加えてもよい。

【００２８】上述した本発明のＮＯｘ吸蔵還元型三元触媒は、無担体でも使用することができるが、自動車の排ガスを浄化するに当たっては、一体構造型担体に担持して用いるのが好ましい。一体構造型担体としては、耐熱性材料から成るモノリス担体が好ましく、例えば、コーディエライトなどのセラミックスやフェライト系ステンレスなどの金属製のものを好適に使用することができる。

【００２９】本発明のＮＯｘ吸蔵還元型三元触媒に係る複合酸化物の製造方法には、例えば、各成分の金属塩（硝酸塩、炭酸塩、クエン酸、塩酸塩など）の水溶液を調製し、場合によってはこれに沈澱剤（アンモニア、炭酸アンモニウムなど）を添加して沈澱物を生成させ、これら溶液又は沈澱物を乾燥、焼成して複合酸化物粉末を得る方法があり、これらの製法により各成分の少なくとも一部が複合化し、目的に合致したものとなる。但し、上記複合酸化物の製造方法は、上記方法に必ずしも限定されるものではなく、上記以外の方法であっても、意図する複合酸化物が形成されれば十分である。

【００３０】上述した本発明のＮＯｘ吸蔵還元型三元触媒は、空燃比が１０～５０の範囲で繰り返し変動するリーンバーンエンジン車の排ガスを浄化するのに好適であり、このような環境下で使用すると、リーン雰囲気でＮＯｘを吸着し、ストイキ又はリッチ雰囲気で、吸着したＮＯｘを還元処理して脱着するため、高いＮＯｘ浄化性能が得られる。更に好適な範囲は、リーン雰囲気が１５～５０で、ストイキ又はリッチ雰囲気が１０～１４．８である。

【００３１】次に、本発明の排気ガス浄化装置につき、図面を参照して詳細に説明する。この排気ガス浄化装置は、上述した本発明のＮＯｘ吸蔵還元型三元触媒を使用した装置である。

【００３２】図１は、本発明に係るＮＯｘ吸蔵還元型三元触媒を用いた排気ガス浄化装置の基本構成の一例を表すブロック図である。同図において、この浄化装置では、内燃機関１の排気系の上流側から、第１空燃比検出手段４、三元触媒２、ＮＯｘ吸蔵還元型三元触媒３、第２空燃比検出手段５が順次配置されている。また、上記空燃比検出手段４及び５に対し、第１空燃比フィードバック手段６ａ及び第２空燃比フィードバック手段６ｂがデータ通信可能に接続されており、第１空燃比フィードバック手段６ａは、第１空燃比検出手段４で検出された排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御し、第２空燃比フィードバック手段６ｂは、燃焼混合気の目標空燃比がリーンからストイキ又はリッチに切り換えられた直後において、第２空燃比検出手段５で検出された排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御する。

【００３３】図２は、本発明に係るＮＯｘ吸蔵還元型三元触媒を用いた排気ガス浄化装置の一例を示すシステム構成図である。なお、図１に示したものと実質的に同一の部材には同一の符号を付し、その説明を省略する。図２において、符号７は燃料噴射弁、８は排気管を示しており、この排気管８を介して、燃料噴射弁７、内燃機関１、三元触媒２を内蔵したケーシング及びＮＯｘ吸蔵還元型三元触媒３を内蔵したケーシングが連通している。また、排気管８には、排気空燃比を検出する第１空燃比センサ４ａ及び第２空燃比センサ５ａが、それぞれ三元触媒２の上流、ＮＯｘ吸蔵還元型三元触媒３の下流に配置されており、第１空燃比センサ４ａ、第２空燃比センサ５ａ及び燃料噴射弁７の出力は、上述した第１空燃比フィードバック手段６ａ及び第２空燃比フィードバック手段６ｂの機能を果たすコントロールユニット６に接続されている。

【００３４】ここで、三元触媒２においては、酸素スト

レージ能力に寄与する成分であるセリア（CeO_2）の量が調整されており、具体的には、従来の三元触媒では、５０～６０ｇ／Ｌであるのに対し、５～３０ｇ／Ｌ、好ましくは５～１５ｇ／Ｌに調整されている。

【００３５】また、ＮＯｘ吸蔵還元型三元触媒３は、上述した本発明に係る触媒であり、排気空燃比がリーンのときに排気ガス中のＮＯｘを吸収し、この吸収したＮＯｘを排気空燃比がストイキ又はリッチのときに還元処理する触媒であり、上述のように、例えばアルミナを担持基材とするが、この担体基材上には、セシウム、カリウムに代表されるアルカリ金属、バリウムに代表されるアルカリ土類金属から選ばれた少なくとも１種と、白金、パラジウム、ロジウムのような貴金属から選ばれた少なくとも１種が担持されている。

【００３６】第１空燃比センサ４ａ及び第２空燃比センサ５ａとしては、排気ガス中の酸素濃度に基づいて排気空燃比を検出するセンサを用いることができるが、理論空燃比のみを検出するストイキセンサであってもよく、また、排気空燃比を広域に検出できる広域空燃比センサであってもよい。

【００３７】コントロールユニット６では、運転条件に応じて目標空燃比を決定し、その目標空燃比の混合気が形成されるように燃料噴射量（噴射パルス幅）が演算され、燃料噴射弁７に対する燃料噴射信号が決定される。なお、目標空燃比としては、ストイキ及びリッチのみならず、リーンも設定することができる構成となっている。

【００３８】また、コントロールユニット６では、通常は第１空燃比センサ４ａで検出される排気空燃比を目標空燃比に近づけるように、例えば、比例積分制御等により、燃料噴射量を補正するための空燃比フィードバック補正係数（操作量）を設定することなどが行われる（この機能が第１空燃比フィードバック手段６ａに相当する。）。なお、目標空燃比のリーンからストイキ又はリッチへの切り換えは、運転条件（加速、負荷・回転の変化）によって行われる他、本来目標空燃比としてリーン空燃比が設定される条件下であっても、ＮＯｘ吸蔵還元型三元触媒３におけるＮＯｘ吸収量が限界値に達していると推定されるときは、一時的にリッチ制御が行える設定になっており、ＮＯｘを還元処理するための一時的なリッチ域への切り換えも含まれる。

【００３９】更に、コントロールユニット６は、目標空燃比がリーンからストイキ又はリッチに切り換えられた直後においては、第２空燃比センサ５ａの出力変化に応じて上記空燃比フィードバック制御を実行するようなっており、この機能は第２空燃比フィードバック手段６ｂが果たす機能に相当する。図３に、かかる第２空燃比フィードバック手段６ｂによるフィードバック制御の一例を示す。

【００４０】図３においては、まず、ステップ１１（以

下、「Ｓ１１」と略す。）で、ＮＯｘを還元処理するための空燃比制御が必要かどうかが判別される。そして、ＮＯｘを還元処理するための空燃比制御が必要であると判断されると、目標空燃比がリーン雰囲気からリッチ雰囲気に切り換えられる（Ｓ１２）。

【００４１】次に、第１空燃比センサ４ａ及び第２空燃比センサ５ａの出力が検出され（Ｓ１３）、第２空燃比センサ５ａの出力が第１空燃比センサ４ａの出力よりリッチであるかどうかが判断される（Ｓ１４）。第２空燃比センサ５ａの出力が第１空燃比センサ４ａの出力よりリッチでない場合には、第２空燃比センサ５ａの出力が第１空燃比センサ４ａの出力よりリッチになるまで空燃比をリッチ化する。そして、第２空燃比センサ５ａの出力が第１空燃比センサ４ａの出力よりリッチになれば、ステップ１５に進み、空燃比をリーンに反転する（図６参照）。

【００４２】上述のステップ１３～１５の処理を行う理由は、以下の通りである。即ち、ＮＯｘ吸蔵還元型三元触媒で還元処理がなされ、ＮＯｘ吸蔵還元型三元触媒からＮＯｘが脱離している間は、空燃比をリッチ化するために供給されたＨＣ及びＣＯにより、それぞれ酸化と還元が行われ、第２空燃比センサ５ａの出力がストイキ近傍に保たれる。その後、ＮＯｘ吸蔵還元型三元触媒から脱離するＮＯｘの量が減少すると、バランスが崩れ、第２空燃比センサ５ａの出力がリッチ方向に動き、第１空燃比センサ４ａと第２空燃比センサ５ａの出力が等しくなった時点でＮＯｘの脱離が終了したと考えられる（図５参照）。しかる後、第２空燃比センサの出力は第１空燃比センサの出力よりリッチになるので、上述の如くリーンへの反転を行えばよいことになる。

【００４３】上述のように、第１空燃比センサ４ａと第２空燃比センサ５ａの出力をもとに目標空燃比をリッチからリーンに反転することにより、リーン運転時にＮＯｘ吸蔵還元型三元触媒が吸収したＮＯｘを十分に脱離させることができる。この際、上流側に配置された三元触媒２に含まれる酸素ストレージ成分であるセリア（CeO_2）を低減させるより、短時間で効果的にＮＯｘを脱離させることが可能になる（図７参照）。また、第１空燃比センサ４ａと第２空燃比センサ５ａの出力をもとに、目標空燃比のリッチからリーンへの反転を行うことで、温度等によりＮＯｘ吸収量が変化したり（図８参照）、経時変化によってＮＯｘ吸収量や酸素ストレージ量に変化があっても、ＮＯｘ吸収量に見合ったＮＯｘの脱離条件を設定することができるようになる。

【００４４】次に、空燃比フィードバック制御の他の例について説明する。図４は、第２空燃比フィードバック手段６ｂによる制御の他の例を示すフローチャートである。同図においては、まず、ステップ２１で、ＮＯｘを還元処理するための空燃比制御が必要かどうかが判別される。かかる空燃比制御が必要であると判断されると、

運転状態（エンジン回転、燃料噴射量）からしきい値Ｓをマップより検出し（Ｓ２２）、次いで、目標空燃比がリーンから理論空燃比又はリッチに切り換えられる（Ｓ２３）。

【００４５】次に、ステップ２４で、第１空燃比センサ４ａ及び第２空燃比センサ５ａの出力を検出し、第２空燃比センサ５ａの出力と第１空燃比センサ４ａの出力の比率がしきい値Ｓ以上になったか否かを判別する（Ｓ２５）。第２空燃比センサ５ａの出力と第１空燃比センサ４ａの出力の比率が、しきい値Ｓより小さい場合には、第２空燃比センサ５ａの出力が第１空燃比センサ４ａの出力よりリッチになるまで空燃比をリッチ化する。第２空燃比センサ５ａの出力と第１空燃比センサ４ａの出力の比率が、しきい値Ｓ以上になったと判断すると、ステップ２６に進み、空燃比をリーンに反転させる（図９参照）。

【００４６】上述のように、本例によれば、図３に示した例と同様に、第１空燃比センサ４ａと第２空燃比センサ５ａの出力をもとに目標空燃比をリッチからリーンに反転することにより、リーン運転時にＮＯｘ吸蔵還元型三元触媒が吸収したＮＯｘを十分に脱離させることができる。また、上流側に配置された三元触媒に含まれる酸素ストレージ成分であるセリア（CeO_2）を低減させるより、短時間で効果的にＮＯｘを脱離させることができるようになる。更に、第１空燃比センサ４ａと第２空燃比センサ５ａの出力の比率をもとに、目標空燃比のリッチからリーンへの反転を行うことで、温度等によりＮＯｘ吸収量が変化したり、経時変化によってＮＯｘ吸収量や酸素ストレージ量に変化があってもＮＯｘ吸収量に見合ったＮＯｘの脱離条件を設定することも可能である。

【００４７】なお、図３及び図４に示した例では、それぞれリッチスパイクの形状を図１０に示したような矩形波としたが、図１１に示すように、リッチスパイクの形状を三角波にしても、上述と同様な効果が得られる。

【００４８】

【実施例】以下、本発明を実施例、比較例及び試験例により詳細に説明するが、本発明はこれら実施例に限定されるものではない。

【００４９】

（１）ＮＯｘ吸蔵還元型三元触媒の製造及び特性試験

（実施例１）硝酸パラジウム水溶液をに活性アルミナ粉末に含浸し、乾燥後、空気中４００℃で１時間焼成して、パラジウム担持アルミナ粉末（粉末Ａ）を得た。この粉末のパラジウム濃度は５．６重量％であった。また、炭酸ランタンと炭酸コバルトの混合物にクエン酸を加え、乾燥後、７００℃で焼成し、粉末（粉末Ｂ）を得た。この粉末は金属原子比でランタン／コバルト＝０．８／１であった。上述のようにして得られた粉末Ａ６００ｇ、粉末Ｂ３００ｇ、水９００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００５０】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、空気中４００℃で１時間焼成し、コート層重量１５０ｇ／Ｌ－担体を得た。得られた１５０ｇ／Ｌ－担体に酢酸バリウム水溶液を含浸し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、炭酸バリウムを担持した実施例１の触媒を得た。このようにして得られた本例の触媒のバリウム量は酸化物換算で２０ｇ／Ｌであった。

【００５１】本例並びに以下の実施例及び比較例の触媒の組成は、表１にまとめて示す。

【００５２】（比較例１）粉末Ｂを活性アルミナに代えた以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５３】（比較例２）バリウム担持を行わなかった以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５４】（実施例２）粉末ＢのＬａをＣｅとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５５】（実施例３）粉末ＢのＬａをＮｄとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５６】（実施例４）粉末ＢのＣｏをＭｎとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５７】（実施例５）粉末ＢのＣｏをＦｅとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５８】（実施例６）粉末ＢのＣｏをＮｉとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００５９】（実施例７）ＢａをＫとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００６０】（実施例８）ＢａをＳｒとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００６１】（実施例９）ＢａをＣｓとした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００６２】（実施例１０）ＢａをＣｓとＭｇの混合物（酸化物換算の重量比で１：１）とした以外は、実施例１と同様の操作を繰り返し、本例の触媒を得た。

【００６３】（実施例１１）硝酸ロジウム水溶液を活性アルミナに含浸し、乾燥後、空気中４００℃で１時間焼成して、ロジウム担持粉末（粉末Ｃ）を得た。この粉末のロジウム濃度は２．０重量％であった。ジニトロジアンミン白金水溶液を活性アルミナに含浸し、乾燥後、空気中４００℃で１時間焼成して、白金担持粉末（粉末Ｄ）を得た。この粉末の白金濃度は４．０重量％であっ

た。上述のようにして得られた粉末Ｃ１０６ｇ、粉末Ｄ２６５ｇ、粉末Ｂ３００ｇ、活性アルミナ粉末２２９ｇ、水９００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００６４】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、４００℃で１時間焼成し、コート層重量１５０ｇ／Ｌ－担体を得た。得られた１５０ｇ／Ｌ－担体に酢酸バリウム水溶液を含浸し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、炭酸バリウムを担持した実施例１１の触媒を得た。このようにして得られた本例の触媒のバリウム量は酸化物換算で２０ｇ／Ｌであった。

【００６５】

【表１】

	貴金属 g/L	複合酸化物組成		炭酸塩元素
		元素	α	
実施例1	Pd＝5.6	La, Co	0.8	Ba
比較例1	↑	なし	↑	Ba
比較例2		La, Co		なし
実施例2		Ce, Co		Ba
実施例3		Nd, Co		Ba
実施例4		La, Mn		Ba
実施例5		La, Fe		Ba
実施例6		La, Ni		Ba
実施例7		La, Co		K
実施例8		↑		Sr
実施例9				Cs
実施例10				Cs+Mg
実施例11	Pt＝1.77 Rh＝0.35			Ba

【００６６】（触媒特性試験１）上述のようにして得られた各例の触媒につき、下記の方法で試験を行った。得られた結果を表２に示す。

（耐久方法）排気量４４００ｃｃのエンジンの排気系に各例の触媒を装着し、触媒入口温度を７００℃とし、５０時間運転した。

（評価方法）排気量２０００ｃｃのエンジンの排気系に各例の触媒を装着し、Ａ／Ｆ＝１１．０を１０秒間、Ａ／Ｆ＝２２を３０秒間を交互に繰り返すように運転し、触媒入口温度を３５０℃とし、この切り換え運転１サイクルのトータル転化率を求めた。

【００６７】

【表２】

	転化率%		
	HC	CO	NO
実施例1	95	100	76
比較例1	96	100	48
比較例2	96	100	48
実施例2	96	100	79
実施例3	96	100	76
実施例4	96	100	76
実施例5	96	100	75
実施例6	96	100	77
実施例7	92	100	82
実施例8	96	100	72
実施例9	90	100	83
実施例10	96	100	85
実施例11	95	100	69

【００６８】（実施例１２）硝酸パラジウム水溶液を活性アルミナ粉末に含浸し、乾燥後、空気中４００℃で１時間焼成して、パラジウム担持アルミナ粉末（粉末Ｅ）を得た。この粉末のパラジウム濃度は５．０重量％であ

った。また、炭酸ランタンと炭酸バリウムと炭酸コバルトの混合物にクエン酸を加え、乾燥後、７００℃で焼成し、粉末（粉末Ｆ）を得た。この粉末は金属原子比でランタン／バリウム／コバルト＝２／７／１０であった。更に、ジニトロジアンミン白金水溶液を粉末Ｆに含浸し、乾燥後、空気中４００℃で１時間焼成して、白金担持粉末Ｆ（粉末Ｇ）を得た。この粉末の白金濃度は、５．０重量％であった。上述のようにして得られた粉末Ｅ５４４ｇ、粉末Ｇ３４２ｇ、活性アルミナ粉末１２ｇ、水９０２ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００６９】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、コート層重量１０５ｇ／Ｌを担持した実施例１２の触媒を得た。このようにして得られた本例の触媒は、触媒１Ｌ当たり、粉末Ｅを６４ｇ、粉末Ｇを４０ｇ含有する。なお、本例並びに以下の実施例及び比較例の触媒の組成は、表３にまとめて示す。

【００７０】（比較例３）実施例１２と同様の操作を行い、パラジウム担持アルミナ粉末（粉末Ｅ）を得た。また、ジニトロジアンミン白金水溶液を活性アルミナ粉末に含浸し、乾燥後、空気中４００℃で１時間焼成して、白金担持アルミナ粉末（粉末Ｈ）を得た。この粉末の白金濃度は、５．０重量％であった。上述のようにして得られた粉末Ｅ５４４ｇ、粉末Ｈ３４２ｇ、活性アルミナ粉末１２ｇ、水９０２ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００７１】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、コート層重量１０５ｇ／Ｌを担持した比較例３を得た。このようにして得られた本例の触媒は、触媒１Ｌ当たり、粉末Ｅを６４ｇ、粉末Ｈを４０ｇ含有する。

【００７２】（実施例１３）粉末Ｅを２７２ｇ、粉末Ｇを１７１ｇ、活性アルミナ粉末を４５６ｇ、水を８９８ｇとした以外は、実施例１２と同様の操作を繰り返し、コート層重量２１０ｇ／Ｌを担持した実施例１３を得た。このようにして得られた本例の触媒は、触媒１Ｌ当たり、粉末Ｅを６４ｇ、粉末Ｆを４０ｇ含有する。

【００７３】（実施例１４）硝酸パラジウム水溶液を活性アルミナ粉末に含浸し、乾燥後、空気中４００℃で１時間焼成して、パラジウム担持アルミナ粉末（粉末Ｅ’）を得た。この粉末Ｅ’のパラジウム濃度は２．５重量％であった。また、ジニトロジアンミン白金水溶液を粉末Ｆに含浸し、乾燥後、空気中４００℃で１時間焼成し、白金担持アルミナ粉末（粉末Ｇ’）を得た。この粉末Ｇ’の白金濃度は、２．５重量％であった。上述のようにして得られた粉末Ｅ’５４５ｇ、粉末Ｇ’３４３ｇ、活性アルミナ粉末２４ｇ、水８８８ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００７４】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、コート層重量２１０ｇ／Ｌを担持した実施例１４を得た。このようにして得られた本例の触媒は、触媒１Ｌ当たり、粉末Ｅ’を１２５ｇ、粉末Ｇ’を７９ｇ含有する。

【００７５】（実施例１５）粉末Ｅ’を３６３ｇ、粉末Ｇ’を２２９ｇ、活性アルミナ粉末を３０８ｇ、水を９００ｇとした以外は、実施例１４と同様の操作を繰り返し、コート層重量３１５ｇ／Ｌを担持した実施例１５を得た。このようにして得られた本例の触媒は、触媒１Ｌ当たり、粉末Ｅ’を１２７ｇ、粉末Ｇ’を８０ｇ含有する。

【００７６】（実施例１６）粉末ＦのＢａをＣｓとした以外は、実施例１５と同様の操作を繰り返し、本例の触媒を得た。

【００７７】（実施例１７）硝酸ロジウム水溶液を活性アルミナ粉末に含浸し、乾燥後、空気中４００℃で１時間焼成して、ロジウム担持アルミナ粉末（粉末Ｉ）を得た。この粉末ＩのＲｈ濃度は４．０重量％であった。得られた粉末Ｉ３３ｇ、粉末Ｅ’４２２ｇ、粉末Ｇ’２２９ｇ、活性アルミナ粉末１９０ｇ、水９２４ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００７８】このスラリー液をコーディライト質モノリス担体（１．３Ｌ、４００セル）に付着させ、空気流にてセル内の余剰のスラリーを除去し、１３０℃で乾燥した後、空気中４００℃で１時間焼成して、コート層重量３１５ｇ／Ｌを担持した実施例１７を得た。

【００７９】（実施例１８）粉末ＦのＢａをＣｓとした以外は、実施例１７と同様の操作を繰り返し、本例の触媒を得た。

【００８０】

【表３】

	貴金属	貴金属量(g/L)	コート層重量(g/L)	炭酸塩元素
実施例12	Pd、Pt	Pd=3.2 Pt=2.0	105	La、Ba、Co
比較例3	Pd、Pt	Pd=3.2 Pt=2.0	105	La、Ba、Co
実施例13	Pd、Pt	Pd=3.2 Pt=2.0	210	La、Ba、Co
実施例14	Pd、Pt	Pd=3.2 Pt=2.0	210	La、Ba、Co
実施例15	Pd、Pt	Pd=3.2 Pt=2.0	315	La、Ba、Co
実施例16	Pd、Pt	Pd=3.2 Pt=2.0	315	La、Cs、Co
実施例17	Pd、Pt、Rh	Pd=3.8 Pt=2.0 Rh=0.5	315	La、Ba、Co
実施例18	Pd、Pt、Rh	Pd=3.8 Pt=2.0 Rh=0.5	315	La、Cs、Co

【００８１】（触媒特性試験２）上述のようにして得られた実施例１２～１７及び比較例３の触媒につき、下記の方法で試験を行った。得られた結果を表４に示す。なお、表４における数字は、いずれも百分率で表されたものである。

（耐久方法）試験例１と同一の方法を行った。

（評価方法）試験例１と同一の方法を行った。

【００８２】

【表４】

	HC	CO	NOx
実施例12	95	100	72
比較例3	93	100	45
実施例13	96	100	78
実施例14	96	100	82
実施例15	97	100	84
実施例16	94	100	92
実施例17	97	100	88
実施例18	95	100	94

【００８３】（２）ＮＯｘ吸蔵還元型三元触媒を用いた排気ガス浄化装置の性能試験

（実施例１９）バリウムをセシウムに代えた以外は、実施例１１と同様の操作を繰り返し、本例の触媒を得た。

【００８４】（実施例２０）まず、活性アルミナ粉末にセリウム８重量％、ジルコニウム４重量％、ランタン４重量％を担持焼成し、セリウム・ジルコニウム・ランタン・アルミナ粉末を得た。この粉末を攪拌しながら硝酸パラジウム水溶液を噴霧し、その後焼成してパラジウム１．１６重量％を担持したパラジウム担持アルミナ粉末を得た。このようにして得られたパラジウム担持アルミナ粉末９００ｇ及び硝酸酸性アルミナゾル９００ｇと酢酸１０重量％水溶液１２００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００８５】このスラリー液をコーディライト質モノリス担体に塗布し、空気流にてセル内の余剰のスラリーを取り除いて乾燥し、４００℃で１時間焼成し、コート層重量１４２ｇ／Ｌのモノリス担体を得た。

【００８６】次に、活性アルミナ粉末に硝酸ロジウム水溶液を噴霧し、その後焼成してロジウム１．０重量％を担持したロジウム担持アルミナを得た。このようにして得られたロジウム担持アルミナ粉末１１４ｇ、上記パラジウム担持アルミナ粉末２７９ｇ及び硝酸酸性アルミナゾル４００ｇと酢酸１０重量％水溶液９００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００８７】このスラリー液を上記コート層重量１４２ｇ／Ｌのモノリス担体に塗布し、空気流にてセル内の余剰のスラリーを取り除き、乾燥した後、４００℃で１時間焼成し、コート層重量２１３ｇ／Ｌを担体した実施例２０を得た。

【００８８】（実施例２１）セリウム８重量％をセリウム４重量％に代えた以外は、実施例２０と同様の操作を繰り返し、本例の触媒を得た。

【００８９】（実施例２２）まず、活性アルミナ粉末に硝酸パラジウム水溶液を噴霧し、その後焼成してパラジウム１．１９重量％を担持したパラジウム１．１９重量％担持アルミナ粉末を得た。これとは別に、硝酸ジルコニウムと硝酸セリウムを含む水溶液にアンモニア水溶液を添加し、生成した沈殿物を焼成して、ジルコニア・セリウム複合酸化物を得た。このようにして得られたパラジウム１．１９重量％担持アルミナ粉末７７２ｇ及びジルコニア・セリウム複合酸化物２１４ｇと酢酸１０重量％水溶液１２００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００９０】このスラリー液をコーディライト質モノリス担体に塗布し、空気流にてセル内の余剰のスラリーを取り除いて乾燥し、４００℃で１時間焼成し、コート層重量１４０ｇ／Ｌのモノリス担体を得た。

【００９１】次に、活性アルミナ粉末に硝酸ロジウム水溶液を噴霧し、その後焼成してロジウム１．０重量％を担持したロジウム担持アルミナを得た。これとは別に、

活性アルミナ粉末に硝酸パラジウム水溶液を噴霧し、その後焼成してパラジウム１．０７重量％を担持したパラジウム１．０７重量％担持アルミナ粉末を得た。このようにして得られたロジウム担持アルミナ粉末１１４ｇ、パラジウム１．０７重量％担持アルミナ粉末３０６ｇ及び上記ジルコニア・セリウム複合酸化物２４０ｇと酢酸１０重量％水溶液９００ｇを磁性ボールミルに投入し、混合粉砕してスラリー液を得た。

【００９２】このスラリー液を上記コート層重量１４０ｇ／Ｌのモノリス担体に塗布し、空気流にてセル内の余剰のスラリーを取り除き、乾燥した後、４００℃で１時間焼成し、コート層総重量２１０ｇ／Ｌを担持した実施例２２を得た。

【００９３】（比較例４）ジルコニア・セリウム複合酸化物２１４ｇをジルコニア・セリウム複合酸化物４２８ｇに代え、上記ジルコニア・セリウム複合酸化物２４０ｇを上記ジルコニア・セリウム複合酸化物４８０ｇに代えた以外は、実施例２２と同様の操作を繰り返し、本例の触媒を得た。

【００９４】（比較例５）ジルコニア・セリウム複合酸化物２１４ｇをジルコニア・セリウム複合酸化物０ｇに代え、上記ジルコニア・セリウム複合酸化物２４０ｇを上記ジルコニア・セリウム複合酸化物０ｇに代えた以外は、実施例２２と同様の操作を繰り返し、本例の触媒を得た。

【００９５】（装置性能試験）上述のようにして得られた実施例１、９、１１及び１９～２２並びに比較例４及び５の触媒につき、下記の方法で試験を行った。得られた結果を表５に示す。

（耐久方法）排気量４４００ｃｃのエンジンの排気系に各例の触媒を装着し、触媒入口温度を７００℃とし、５０時間運転した。

（評価方法）排気量２０００ｃｃのエンジンの排気系の同一流路中に、表５に示すように触媒を２個装着し、Ａ／Ｆ＝１１．０、Ａ／Ｆ＝２２を交互に繰り返すように運転し、触媒入口温度を上流側４５０℃、下流側３５０℃とし、この切り換え運転１サイクルのトータル転化率を求めた。

【００９６】

【表５】

	三元触媒	ＮＯｘ吸蔵還元型三元触媒	ηＨＣ（％）	ηＮＯｘ（％）
比較例６	比較例４	実施例９	９８	７８
実施例２３	実施例２０	実施例９	９８	８８
実施例２４	実施例２１	実施例９	９８	９２
実施例２５	実施例２２	実施例９	９７	８５
比較例７	比較例５	実施例９	８５	９０
実施例２６	実施例２１	実施例１	９８	８４
実施例２７	実施例２１	実施例１１	９５	９０
実施例２８	実施例２１	実施例１９	９５	８８

【００９７】表５の結果から、セリア及びセリアを含む複合酸化物の量が触媒１リットル当たり５～３０ｇである三元触媒を使用した場合（実施例２３～２８）は、ＨＣの転化率及びＮＯｘの転化率はいずれも良好であるのに対し、セリア及びセリアを含む複合酸化物の量が触媒１リットル当たり３０ｇより多い三元触媒を使用した場合（比較例６）には、ＨＣの転化率は良好であるが、ＮＯｘの転化率が低下し、セリア及びセリアを含む複合酸化物の量が触媒１リットル当たり５ｇより少ない三元触媒を使用した場合（比較例７）には、ＮＯｘの転化率は良好であるが、ＨＣの転化率が低下することがわかった。

【００９８】

【発明の効果】以上説明してきたように、本発明によれば、所定の複合酸化物と貴金属元素とを適切に共存させることなどしたため、リーン雰囲気でのＮＯｘ浄化性能に優れるＮＯｘ吸蔵還元型三元触媒を提供することができる。

【００９９】また、本発明によれば、ＮＯｘ吸蔵還元型三元触媒の上流側に配置された三元触媒中の酸素ストレージ能力に寄与する成分の量を低減することなどしたため、排気空燃比がリーンからリッチに切り換わった際にＮＯｘ吸蔵還元型三元触媒に十分なＨＣ及びＣＯが供給できるようになり、ＮＯｘの浄化率が向上する排気ガス浄化装置を提供することができる。

【０１００】更に、本発明によれば、排気空燃比に基づいて燃焼混合気の空燃比を目標空燃比にフィードバック制御する空燃比フィードバック手段を設けることなどをしたため、ＨＣ及びＣＯの浄化性能の悪化を最小限に抑えることができる排気ガス浄化装置を提供することも可能となる。

【０１０１】

【図面の簡単な説明】

【図１】本発明に係るＮＯｘ吸蔵還元型三元触媒を用いた排気ガス浄化装置の基本構成の一例を表すブロック図である。

【図２】本発明に係るＮＯｘ吸蔵還元型三元触媒を用いた排気ガス浄化装置のシステムの一例を表す構成図であ

る。

【図３】請求項８に係る排気ガス浄化装置の第２空燃比フィードバック手段による制御の一例を示すフローチャートである。

【図４】請求項９に係る排気ガス浄化装置の第２空燃比フィードバック手段による制御の一例を示すフローチャートである。

【図５】空燃比センサ出力とＮＯｘの脱離状態を示す図である。

【図６】図３を実施した場合における空燃比制御の一例を示す図である。

【図７】セリアＣｅＯ$_2$の量とＮＯｘの脱離状態との関係を示す図である。

【図８】排気ガス温度によるＮＯｘ吸収量の変化を示す図である。

【図９】図４を実施した場合における空燃比制御の一例を示す図である。

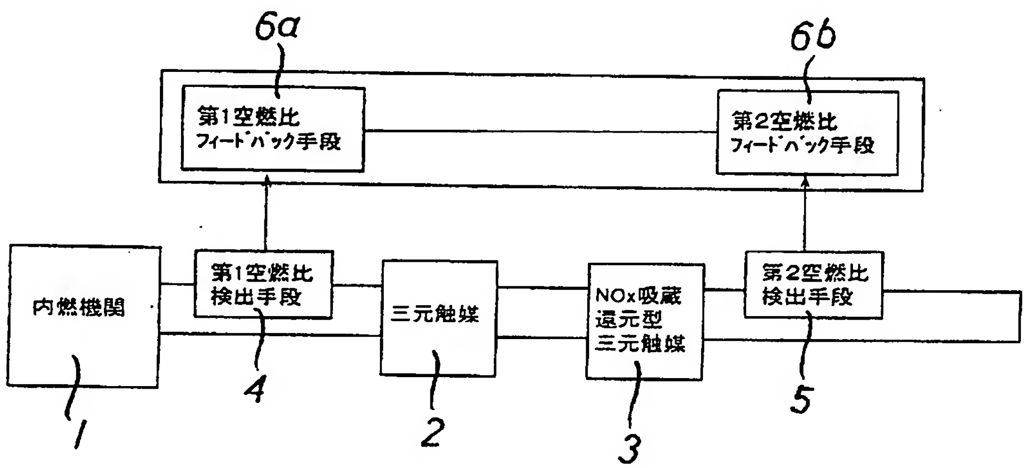
【図１０】図３及び図４における空燃比制御の波形を示す図である。

【図１１】空燃比制御の波形の一例を示す図である。

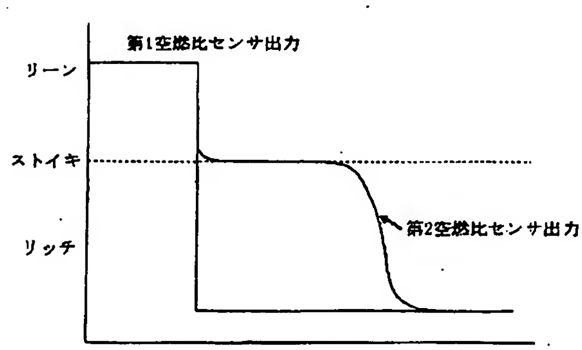
【符号の説明】

1	内燃機関
2	三元触媒
3	ＮＯｘ吸蔵還元型三元触媒
4	第１空燃比検出手段
4 a	第１空燃比センサ
5	第２空燃比検出手段
5 a	第２空燃比センサ
6	コントロールユニット
6 a	第１空燃比フィードバック手段
6 b	第２空燃比フィードバック手段
7	燃料噴射弁
8	排気管

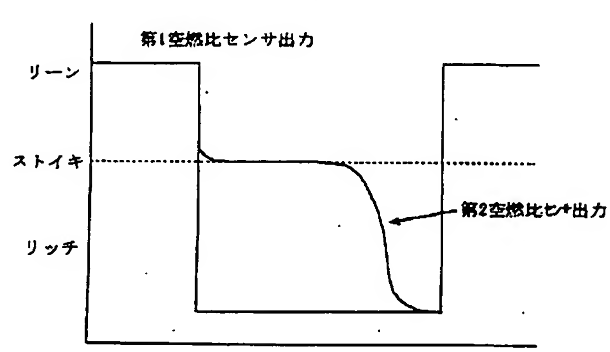
【図１】



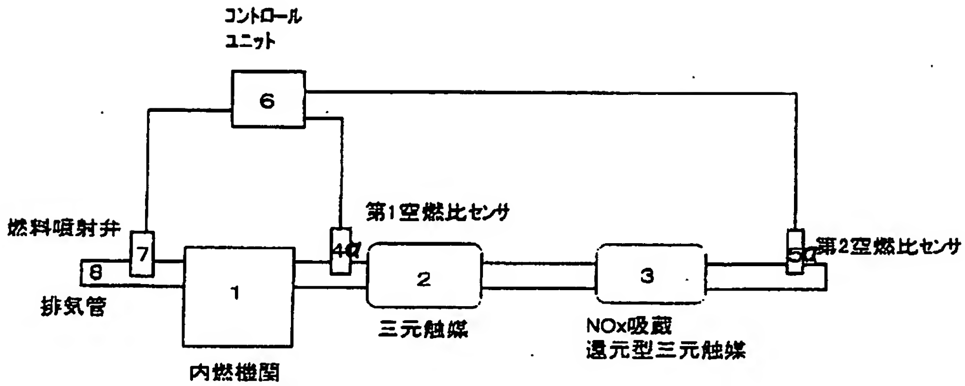
【図５】



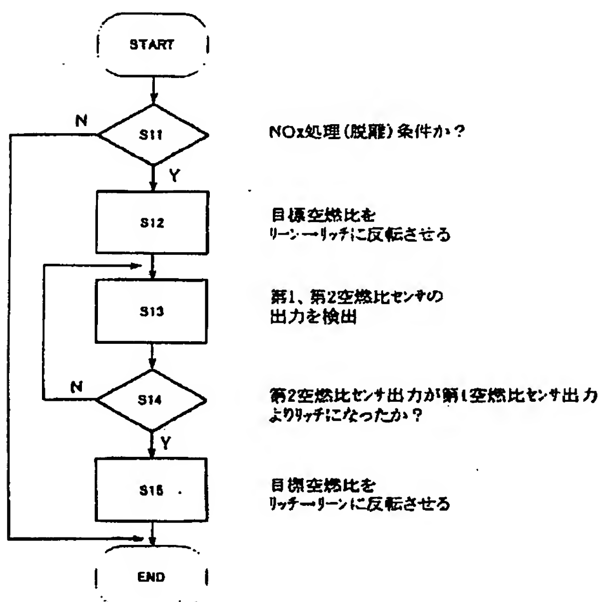
【図６】



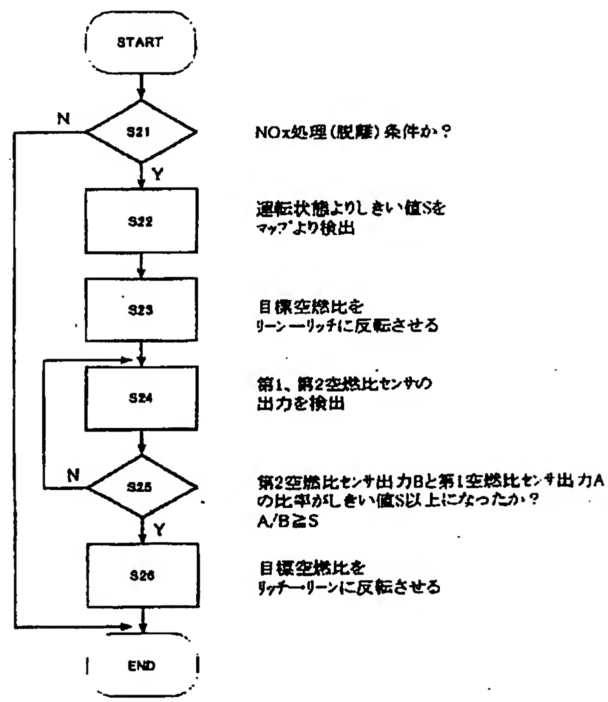
【図2】


コントロール
ユニット
6
燃料噴射弁
7
8
排気管
1
内燃機関
第1空燃比センサ
4
2
三元触媒
3
NOx吸蔵
還元型三元触媒
5
第2空燃比センサ

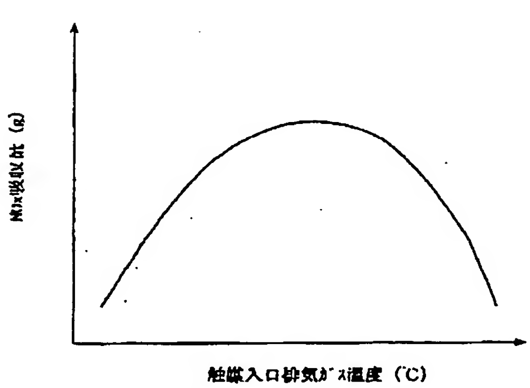
【図3】


START
S11
NOx処理(脱離)条件か？
N
Y
S12
目標空燃比を
リーン→リッチに反転させる
S13
第1、第2空燃比センサの
出力を検出
S14
第2空燃比センサ出力が第1空燃比センサ出力
よりリッチになったか？
N
Y
S15
目標空燃比を
リッチ→リーンに反転させる
END

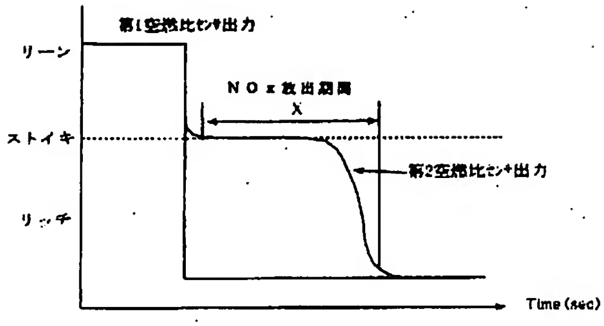
【図4】

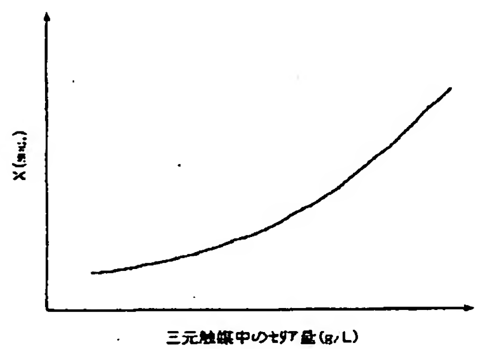

START
S21
NOx処理(脱離)条件か？
N
Y
S22
運転状態よりしきい値Sを
マップより検出
S23
目標空燃比を
リーン→リッチに反転させる
S24
第1、第2空燃比センサの
出力を検出
S25
第2空燃比センサ出力Bと第1空燃比センサ出力A
の比率がしきい値S以上になったか？
A/B≧S
N
Y
S26
目標空燃比を
リッチ→リーンに反転させる
END

【図8】

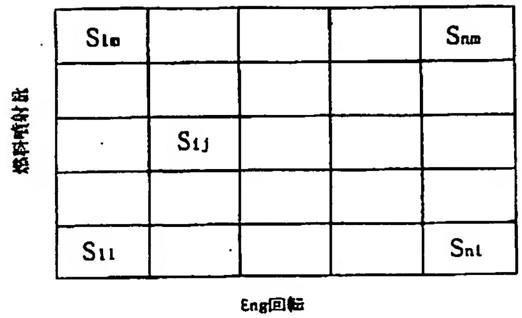

NOx吸収比（g）
触媒入口排気ガス温度（℃）

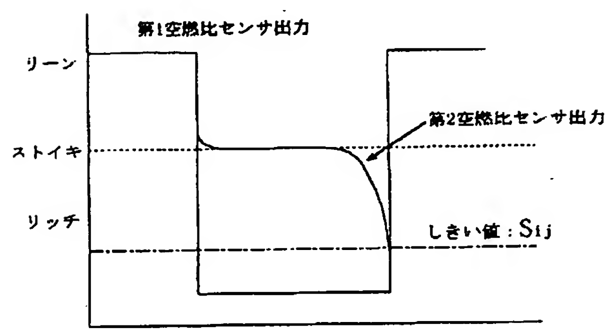
【図７】



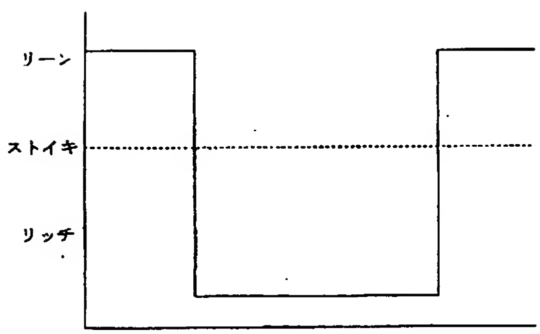


【図９】

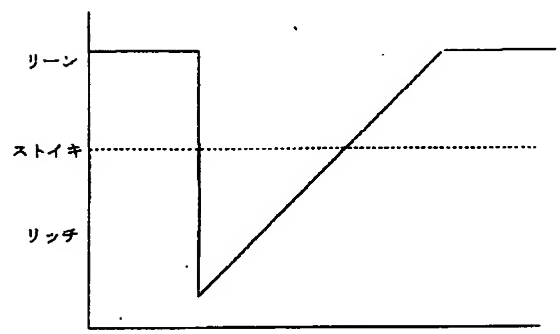




【図１０】



【図１１】



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